공학석사학위논문

Study of Acid Leaching of Rare Earth Elements Ore from Mushgai Khudag Area, Mongolia

몽골 무시가이쿠닥 희토류 광석의 산 침출 특성에 대한 연구

2014 년 2 월

서울대학교 공과대학원

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이 논문을 공학석사학위논문으로 제출함

2013 년 12 월

서울대학교 대학원

에너지시스템공학부

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2014 년 1 월

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Abstract

In 2010, reduction of Rare Earth Elements (REE) exports quota of China, and the dispute between China and Japan caused a dramatic increase in REE prices. Therefore, it is important to obtain a stable supply of REE globally, as problems with increasing REE prices in Korea are serious. When REE prices were low, the REE product processing technology had not yet been developed in Korea. Instead, Korea imported finished or half-finished REE products from other countries. Although REE prices are currently relatively stable, they can soar again. Thus, Korea needs to prepare countermeasures for resources security, and a R&D project was set up to explore REE deposits. As part of the R&D project, this study looks at the acid leaching of REE ore. The REE ore sample was collected from the High Grade Zone (HGZ), which is in the Mushgai Khudag area of Mongolia. The total REE content was relatively high at approximately 10 %, so if adequate processing technologies are available, a mass supply of REE to Korea can be possible

For optimum leaching conditions, experiments were performed at various settings where sulfuric, hydrochloric, and nitric acid were used as leaching reagents. The leaching experiments were performed utilizing 3 reagents to determine the basic leaching characteristics of leaching reaction and optimum leaching time. Additionally, the optimum leaching reagent and its concentration were identified through leaching

experiments that changed the leaching reagent concentrations.

After the leaching time, reagent, and concentration were determined, the leaching experiments were conducted to improve the REE leaching levels. Generally, chemical reaction rates can be sped up at higher temperatures. Thus, experiments were conducted at low leaching reagent concentrations at elevated temperatures. Fe was removed in the leachate by using magnetic separated samples. If there is a large amount of Fe in the leachate, the process cost can increase. In addition, the particle size change in the leaching experiment was studied. At an optimum particle size, target materials can be extracted efficiently due to the enhanced liberation degree. At an adequate solid to liquid ratio, optimum leaching levels are obtained so that an economical amount of leaching reagent can be determined.

As a result, when 2.0 M of hydrochloric acid or nitric acid was used, more than 90 % REE leached out in an hour. However, when sulfuric acid was used, 70 ~ 80 % REE leached out even at high acidic concentrations of 13.0 M due to sulfate formation. The optimum leaching conditions were identified using 2.0 M hydrochloric acid with a leaching time of 1 ~ 2 hours. The optimum temperature was 25 ℃ as it was determined there is no benefit in operating at a higher temperature. The optimum particle size was 90 % passing 50 mesh, since there was no big difference in the REE leaching levels at a finer particle size. The optimum pulp density to leach REE was 10 ~ 15 %, because at 25 %, most of the

REE disappeared and leaching levels of some impurities were high. Thus, the impurities can be removed by solid-liquid separation.

Keywords: REE, acid leaching, apatite, magnetic separation
Student Number: 2011-21090

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1. Introduction

1.1. Research background

Rare Earth Elements (REE), oft known as the 'vitamin of industry,' are significant materials used for the modern high-tech industry. The elements are used for many applications like computers, mobile phones, optical glasses, phosphors, lasers, etc. However, China, which produces 97 % of the REE in the world, announced a reduction in the export quota of REE in July 2010. In September 2010, China declared a REE export ban to Japan after a dispute over the Senkaku Islands between China and Japan. As a result, China's export restraints on REE caused a spike in prices and raised fears of an unstable supply (Hong, 2012). Therefore, it became imperative to obtain a stable supply of REE throughout the whole world especially as the importance of REE is rising in Korea.

REE refer to the fifteen metallic elements in the lanthanide series (atomic numbers 57 ~ 71) with the chemically similar yttrium (39), and occasionally scandium (21) (Gupta et al., 1992). They are divided into two or three groups; in two groups, atomic numbers 57 through 63 (La ~ Eu) are "Light REE (LREE)" and 64 through 71 (Gd ~ Lu) and 39 (Y) are "Heavy REE (HREE)." For 3 groups, 57 ~ 60 (La ~ Nd) are LREE, 61 ~ 64 (Pr ~ Gd) are "Medium REE (MREE)," and 65

~ 71 (Tb ~ Lu) and 39 (Y) are HREE. Scandium, when it is classified as a REE, is not included in either the LREE or HREE classifications (Gupta et al., 1992).

Unlike as is referenced by the name, REE are not rare, because they were named before technology had been developed. The amount of the rarest REE in the Earth's crust is greater than that of precious metals like gold or platinum. The total rare earth oxide (TREO) concentration in the crust is about 220 ppm, which is more than the 200 ppm concentration of carbon. Ce is the 25th most abundant element at 68 ppm and is similar to copper (Anderson et al., 2011).

Recently, there have been confirmed REE reserves of 88 million tons worldwide with possible reserves up to 150 million tons. China is known to have 30.9 % of the confirmed reserves and 57.71 % of possible reserves, which is then followed by the Commonwealth of Independent States (CIS), US, Australia, India, Brazil, and Malaysia (Kim, 2011). In Figure 1, the world distribution of REE deposits, reserves, and operating mines are shown. Due to environmental problems and mass production of REE in China, REE production outside of China has ceased since the late 1990s.

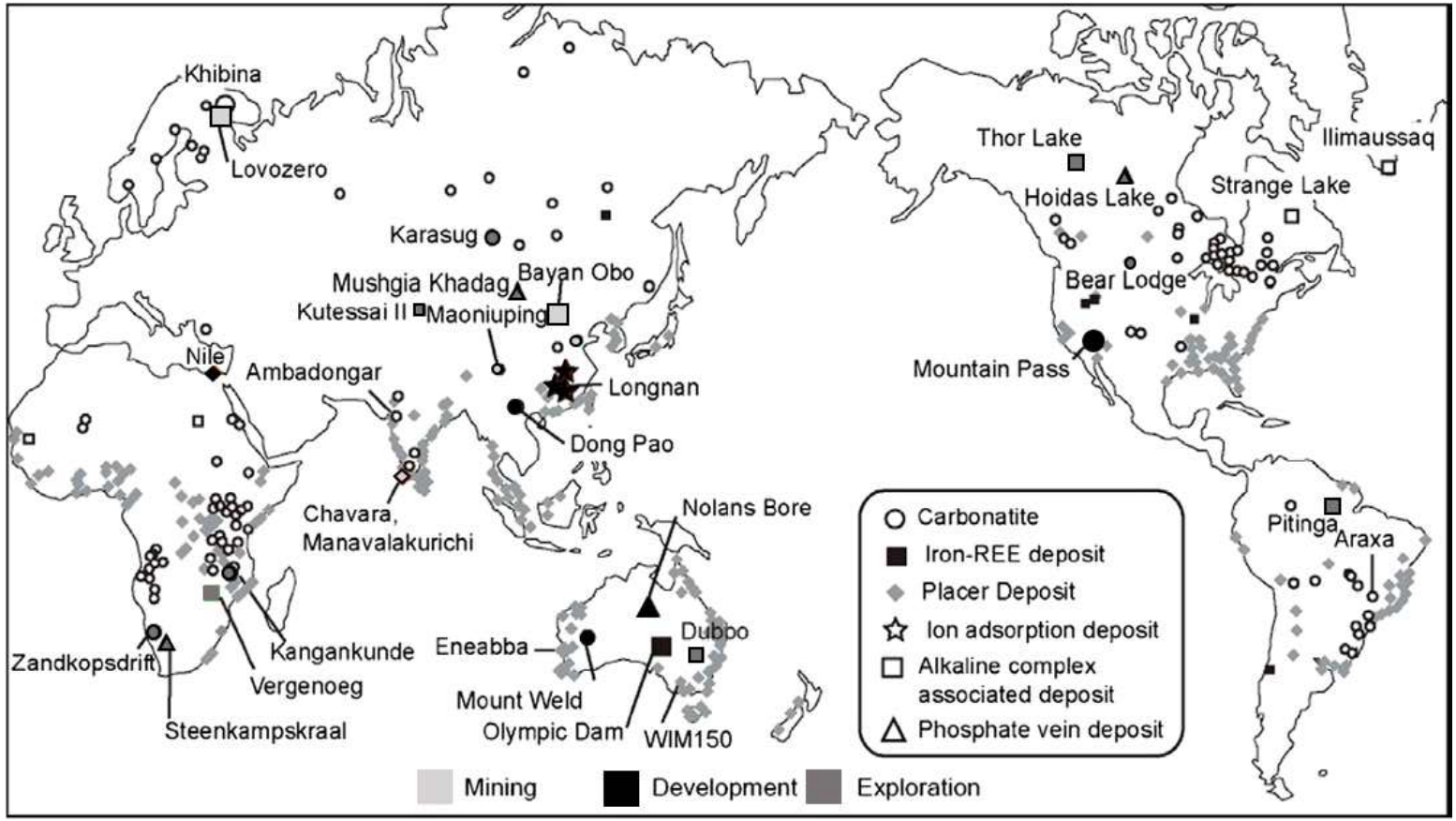

Figure 1. Worldwide distribution of REE deposits, reserves and operating mines (Okuya, 2011)

The side effects of China's REE monopoly are serious since China uses REE as weapon during diplomatic disputes with other countries. China wins the dispute by stopping the REE export as with the case of the Senkaku Islands. Thus, between 2010 and 2011, REE prices soared dramatically (Figure 2). Now, REE prices have decreased to a little higher level than they were in 2010, but countries that import REE cannot rely on China if they want to prevent a similar problem from occurring in the future.

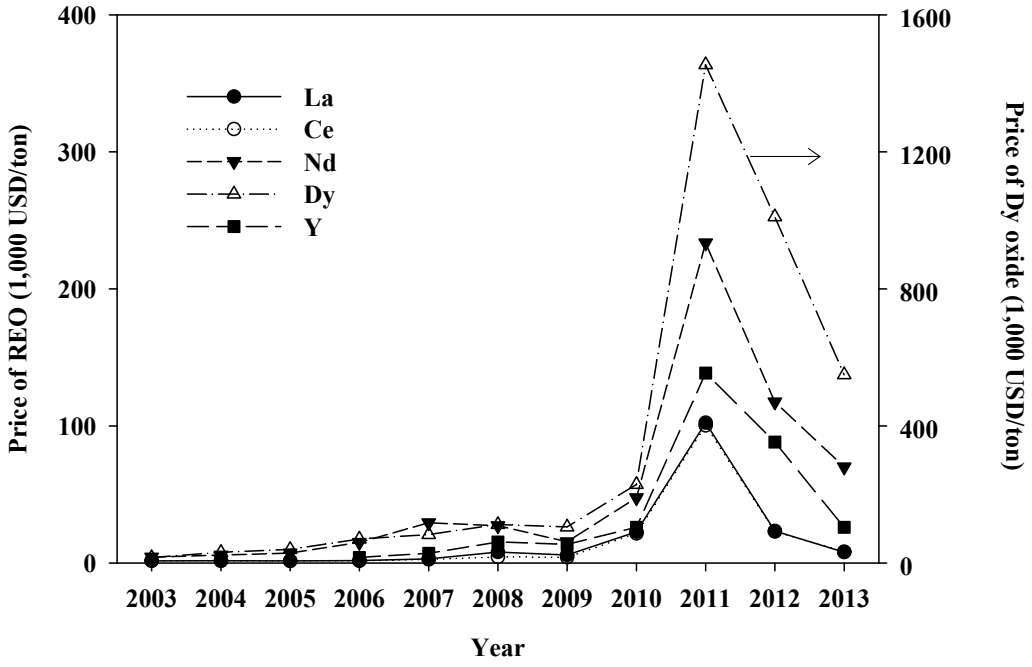

Figure 2. Price of REE in recent 10 years (KORES, 2013)

In Korea, the problems involved with REE prices increases are more serious. When REE prices were cheap, the technologies for processing REE products had not yet been developed. Instead, Korea imported finished or half-finished REE products from other countries such as Japan or China, which led to few REE processing technologies in Korea. Thus, the import costs increase more when prices of raw REE materials soar. Although the REE prices are relatively stable now, they can soar again. Therefore, Korea needs to take countermeasures for resources security since there are no economical REE ore deposits within the nation. REE mines in overseas locales and REE processing technologies are crucially needed.

According to a 2009 estimate by the U.S. Geological Survey, Mongolia has 31 million tons of REE reserves, or 16.77 percent of the world's total, which is exceeded only by China. In light of Chinese restrictions, Mongolia has become a leading contender in the new rush for REE resources. At present, Mongolia is planning to massively increase its transportation infrastructure in order to ship mineral resources across the country to Russia's Far East. Therefore, Korea can potentially receive Mongolian resources as a major metal supplier. A R&D project was set up through international collaboration to explore one of the REE deposits in Mongolia.

Every ore deposit has a unique mixture of elements and minerals, requiring the development of a process uniquely

suitable for separating the minerals from each ore deposit. As shown in Figure 3, the exploration, mining, mineral processing, purification of leachate, metal making, and magnet making are currently under process. This study reports on the project with an emphasis on developing an effective leaching method to extract REE from the ore.

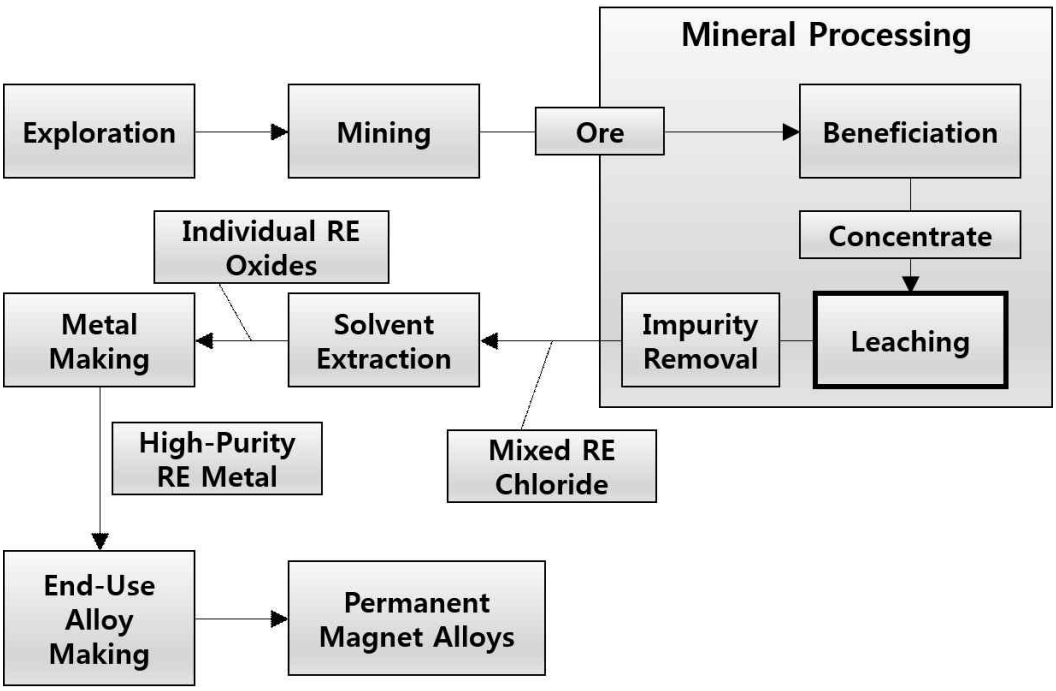

Figure 3. Generalized phases of REE processing for magnet alloy production (Retrieved from homepage of Great Western Minerals Group)

1.2. Recent studies

REE research has been limited in Korea. From the late 1980s to 1990s, monazite ore deposits were discovered Hongcheon, in Gangwon. In 2011, 150 thousand tons of REE ore were confirmed in that location. REE mineral processing research began in the 1990s by Korea Institute of Geoscience and Mineral Resources (KIGAM). In 2004, REE leaching studies using Hongcheon monazite were carried out and extraction of valuable materials from Hongcheon REE ores was tried in 2010 ~ 2011 for government task, but the results of these studies were not commercialized. On the other hand, the US, Australia, China, and other countries conducted a significant amount of research due to the plethora of high grade REE ore deposits. In the recent 20 ~ 30 years, China has been a significant source of research.

There are no economic REE ore deposits in Korea, so overseas REE ore developments have been attempted. One of them is "Mushgai Khudag REE project in Mongolia." From 1980s, studies about geology, mineralization, exploration method were carried out about that area. In the early 1980s, the mineral prospecting study was carried out at Mushgai Khudag by Geological Information Center in Russia, and the Mongolian geological survey team conducted drilling surveys and made geological maps.

Garamjav and Jargalan studied Mongolian REE matellogeny in 2009, while Yoo and Koh, in KIGAM, studied Mushgai

Khudag ore types, in 2011. On-site surveys for R&D projects were carried out by Korea Resources Corporation (KORES) in 2011. From these studies, Mushgai Khudag geology and ore type information was obtained. However, it seemed that hydrometallurgical studies involved in Mushgai Khudag materials were rare.

REE are mainly produced from bastnasite ($R_2(CO)_3F_3$) and monazite (RPO_4) while Y can be produced from xenotime (YPO_4). There are many leaching studies based on these minerals, and common leaching methods were established. Monazite ore undergoes grinding, spiraling, and magnetic separating; the concentration is leached through the concentrated sulfuric acid method or NaOH method. Monazite has been mined in Australia, India, US, and other areas to a lesser degree (Anderson et al., 2011). Bastnasite ore is crushed, ground, classified, and concentrated by flotation, and the concentrated ore undergoes HCl digestion. The residue is reacted with NaOH to produce REE hydroxides, which then repeat HCl leaching. In addition, the ore can be leached with sulfuric acid after oxidization roasting. Bastnasite is primarily mined in the US and China (Anderson et al., 2011).

In this study, the major REE mineral is apatite, which does not yet have a established hydrometallurgical method. However, from the 1950s, studies about REE contained in phosphate rock as well as REE extraction from phosphate rock were conducted. Recently, laboratory studies about REE leaching from Chardormalu apatite was conducted in Iran

(Esmaeil Jorjani et al., 2011). Phosphate rock contains up to 1 % REE oxides present in isomorphous substitution for Ca^{2+} (Habashi, 1985).

1.3. Research purpose

Before China announced a reduction in REE export quota in 2010, REE prices were very low. REE processing technology development was rarely done in Korea as China produces approximately 97 % of the world production of REE. However, the reduction of REE exports quota and the dispute between China and Japan led to increases in prices. The prices have decreased somewhat since then, but are still higher than they were in 2009. In the future, an imbalance between REE supply and demand is expected due to industry developments in developing countries and the application of high-technology associated with REE in advanced countries. Thus, REE prices will remain high, so Korea has to develop overseas REE ore deposits and obtain processing technologies.

REE hydrometallurgical research was performed in this study to derive REE acid leaching. Leaching is the first step for extracting REE from the ore, and the amount of REE extracted in this step determines the amount of REE product. The scope of this study is as follows:

1) First, basic leaching kinetics experiments were conducted. This work is basic to other experiments. The possibility of reaction can be figured out. Also, optimum leaching time can be determined.

2) Leaching level changes were evaluated at various

concentrations of the leaching reagent. Several leaching reagents were used to find the optimal concentrations and types.

3) From the results, the optimum leaching reagent was selected keeping the price in mind. Leaching reagent must extract materials effectively, too. Sulfuric acid, hydrochloric acid, and nitric acid were used as leaching reagents.

4) To improve leaching levels, experiments were performed at different temperatures. Since the reaction rate can increase at higher temperatures, the leaching levels can be improved when temperatures increase. In some cases, increasing the temperature can be more economical than increasing concentration of reagents. Therefore, the temperature effect needs to be studied.

5) The leaching experiments with magnetic separated sample were carried out. REE minerals are usually associated with Fe minerals. Therefore, Fe needs to be removed to improve REE leaching levels and remove impurities. The leaching experiments were done with both raw samples and magnetic separated samples before evaluating the leaching levels and concentrations of REE and Fe in leachate.

6) A study about the changes in leaching levels was conducted as the sample particle size changed. To extract

target materials efficiently, an accurate liberation degree is needed. The smaller the sample particle size, the larger its surface area; thus, contact between the sample and reagent can occur more frequently. However, if the particle size is too small, impurities can be leached out, which means the sample particle size needs to be controlled accurately.

7) Leaching experiments were conducted with pulp density changes. Generally, the lower the pulp density, the higher the leaching levels. However, if the pulp density is too low, the consumption of leaching reagent increases and increases the cost. When there is a high pulp density, the target materials cannot be extracted. Thus, it is important to determine the optimum pulp density.

The final goal of this study is to achieve 80 % leaching levels that lead to the optimum leaching conditions and remove impurities.

2. Background theory

2.1. Chemical properties of REE

REE consist of 17 elements - 15 lanthanide elements from No. 57 to 71 in the periodic table, as shown in Figure 4, lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), and No. 21 scandium (Sc), No. 39 yttrium (Y). The atomic numbers 57 through 71 are similar with lanthanum, so they were named lanthanide. In addition, No. 21 Sc is classified as a REE because its property is similar to lanthanide and Y.

The properties of REE are similar because they have the same number of peripheral electrons. This makes it difficult to separate them from each other. In the past, REE were not separated but made into mixed REE or mischmetal. Recent developments into REE separation and purification show that REE can be separated at very high purity (Kim et al., 2010).

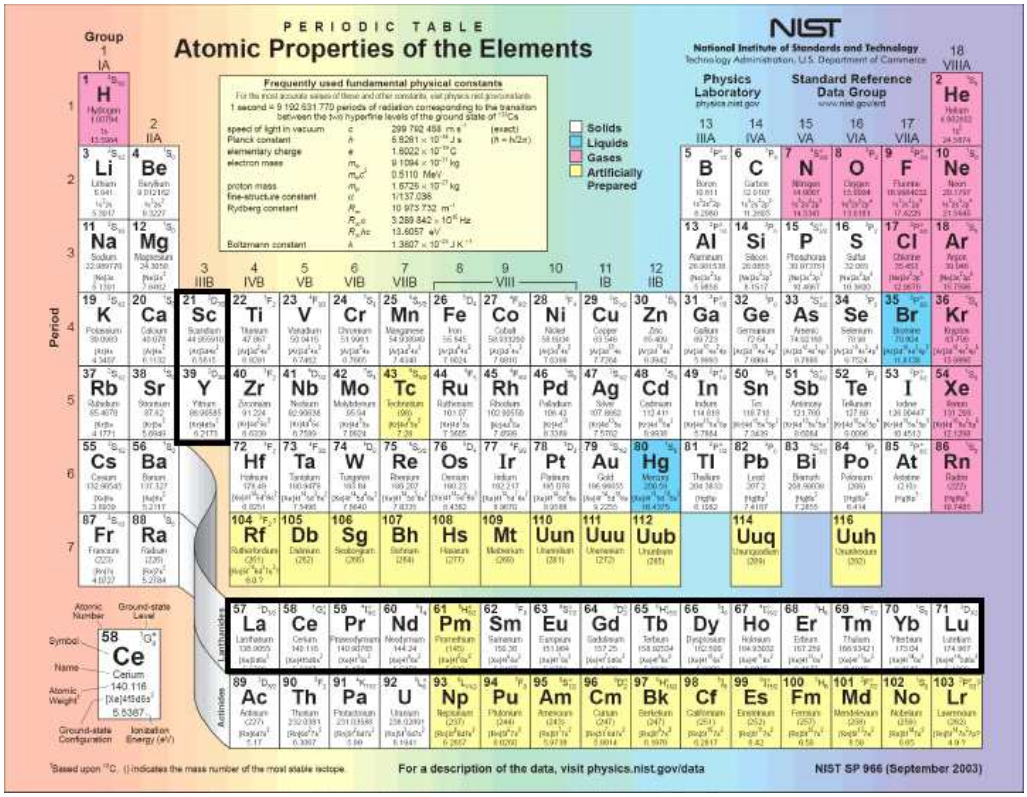

Figure 4. Periodic table

REE can be separated by adjusting the OH^- concentration or adding oxidant / reductants, despite the chemical similarity of these metal ions (Kim et al., 2014). Most of the REE are present in nature in a +3 valance state. However, some REE such as Ce, Pr, and Tb can exist at a +3 or +4 valance state, and other REE such as Sm, Eu, Tm, and Yb are in a +2 or +3 state. These different valance states can be used to separate these elements from others as shown in Figure 5, which shows separated REE metals.

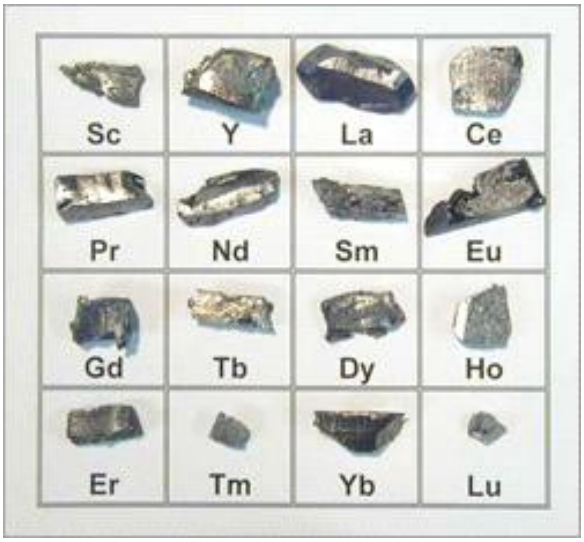

Figure 5. Many kinds of REE metals

In nature, REE exist in over 200 minerals. However, 95 % of REE are found in bastnasite, monazite, and xenotime along with various kinds of REE minerals: patite, cheralite, eudialyte, loparite, phosphorites, rare-earth-bearing (ion adsorption) clays, secondary monazite, and spent uranium solutions.

2.2. Analysis of thermodynamic data

Thermodynamic data (Firsching et al., 1991; Kim et al., 2014; La Iglesia, 2009; Oxtoby et al., 2002) was analyzed to identify the mechanism of REE ore leaching. Through analysis, theoretical leaching pH's were found, and established the experimental pH.

The theoretical leaching pH's of REE phosphates and carbonates as well as apatite were calculated. Such calculations have practical importance since REE occur in nature in association with phosphate, as is the case of the monazite type deposits, carbonate in the bastnasite type (Kim et al., 2014), or apatite ore in the Mushgai Khudag research area.

To calculate the leaching pH, ΔG_f° values of REE phosphates and carbonates, apatite, and REE ions must be known. The ΔG_f° values of apatite, REE ions, and Ca phosphate were found easily, but those of REE phosphates and carbonates were calculated from K_{sp} values.

In Tables 1 and 2, the leaching pH's of REE phosphates and carbonates are shown. The fluorapatite, hydroxyapatite, and Ca phosphate are shown in Tables 3 to 5. Leaching pH's were calculated according to Eq. (1) to (5), where leaching pH's were calculated on the assumption that 0.1 mol/L of REE were dissolved in the solution.

$$RPO_4 + 3H^+ \rightarrow R^{3+} + H_3PO_4 \quad (1)$$

$$R_2(CO_3)_3 + 6H^+ \rightarrow 2R^{3+} + 3H_2CO_3 \quad (2)$$

$$Ca_{10}(PO_4)_6F_2 + 20H^+ \rightarrow 10Ca^{2+} + 6H_3PO_4 + 2HF \quad (3)$$

$$Ca_{10}(PO_4)_6(OH)_2 + 22H^+ \rightarrow 10Ca^{2+} + 6H_3PO_4 + 2H_2O \quad (4)$$

$$Ca_3(PO_4)_2 + 6H^+ \rightarrow 3Ca^{2+} + 2H_3PO_4 \quad (5)$$

From the results in Table 1, REE phosphates can be leached at pH of about −1. The dissolution of REE from phosphates by an acid has been very difficult, requiring very high acid consumption (Kolonin et al., 2008; Shwe et al., 2008), but REE carbonates can be leached more easily than phosphate at pH 2 ~ 4. For apatite, leaching pH varied with type. From Tables 3 and 4, it is shown that fluorapatite could be leached out at pH of about 0.9 and hydroxyapatite at pH of about 2.9. Ca phosphates can be leached at pH 1.8 (Table 5). With this information, effective experimental leaching pH can be determined.

The leaching pH of Ce phosphate and carbonate were not calculated due to lack of data. However, chemical properties of REE are similar, which means that leaching pH may be similar as well.

Table 1. Analysis of thermodynamic data about REE phosphates

REE Phosphates	$\Delta G_f°$ (kcal/mol)					pH
	RPO_4	H^+	R^{3+}	H_3PO_4	$\Delta G°$	
YPO_4	-441.22	0.00	-164.10	-272.94	4.18	-0.69
$LaPO_4$	-453.52	0.00	-174.50	-272.94	6.08	-1.15
$PrPO_4$	-449.20	0.00	-170.30	-272.94	5.95	-1.12
$NdPO_4$	-446.95	0.00	-168.20	-272.94	5.80	-1.09
$SmPO_4$	-445.80	0.00	-167.00	-272.94	5.86	-1.10
$GdPO_4$	-443.78	0.00	-165.80	-272.94	5.04	-0.90

Table 2. Analysis of thermodynamic data about REE carbonates

REE Carbonates	$\Delta G_f°$ (kcal/mol)					pH
	$R_2(CO_3)_3$	H^+	R^{3+}	H_2CO_3	$\Delta G°$	
$Y_2(CO_3)_3$	-749.45	0.00	-164.10	-148.85	-25.30	3.42
$Sc_2(CO_3)_3$	-714.45	0.00	-143.70	-148.85	-19.50	2.72
$La_2(CO_3)_3$	-768.06	0.00	-174.50	-148.85	-27.50	3.69
$Pr_2(CO_3)_3$	-764.13	0.00	-170.30	-148.85	-23.02	3.15
$Nd_2(CO_3)_3$	-761.17	0.00	-168.20	-148.85	-21.78	2.99
$Sm_2(CO_3)_3$	-759.19	0.00	-167.00	-148.85	-21.35	2.94
$Gd_2(CO_3)_3$	-758.21	0.00	-165.80	-148.85	-19.94	2.77

Table 3. Analysis of thermodynamic data about fluorapatite

$\Delta G_f°$(kJ/mol)						pH
$Ca_{10}(PO_4)_6F_2$	H^+	Ca^{2+}	H_3PO_4	HF	ΔG°	
-12885.9	0	-553.58	-1142.54	-296.82	-98.78	0.87

Table 4. Analysis of thermodynamic data about hydroxyapatite

$\Delta G_f°$(kJ/mol)						pH
$Ca_{10}(PO_4)_6(OH)_2$	H^+	Ca^{2+}	H_3PO_4	H_2O	ΔG°	
-12503.5	0	-553.58	-1142.54	-237.18	-361.9	2.88

Table 5. Analysis of thermodynamic data about Ca phosphate

$\Delta G_f°$(kJ/mol)					pH
$Ca_3(PO_4)_2$	H^+	Ca^{2+}	H_3PO_4	ΔG°	
-3884.82	0	-553.58	-1142.54	-61	1.78

2.3. Leaching methods of REE ores

The most typical REE minerals are monazite and bastnasite. Thus, the hydrometallurgical studies about these minerals have been conducted for a long time and established common leaching methods. In this study, the target mineral is apatite. Therefore, to conduct more effective experiments, a case study on the leaching of monazite, bastnasite, and apatite was conducted.

2.3.1. Monazite[19]

For the hydrometallurgical treatment of monazite, a concentrated sulfuric acid method and NaOH method are mainly used. The concentrated sulfuric acid method can be used even for ore contained in low concentrations of REE and large particles. However, sulfuric acid can corrode facilities and lead to environmental problems. It's difficult to recover phosphorus in the ore as well.

The particle sizes of sample must be very fine in the NaOH method. However, the maintenance of facilities is not difficult and environment problems rarely occur. Since it is possible to recover phosphorus, in most monazite processes, the NaOH method is used at normal pressure.

As shown in Figure 6, monazite is first reacted with NaOH to acquire REE hydroxides. At this time, thorium (Th) is changed to be insoluble Th hydroxide, whereas phosphorus is

changed to be soluble sodium phosphate as shown in Eq. (6) and (7). Then, the REE hydroxides are leached with HCl (Eq. (8)).

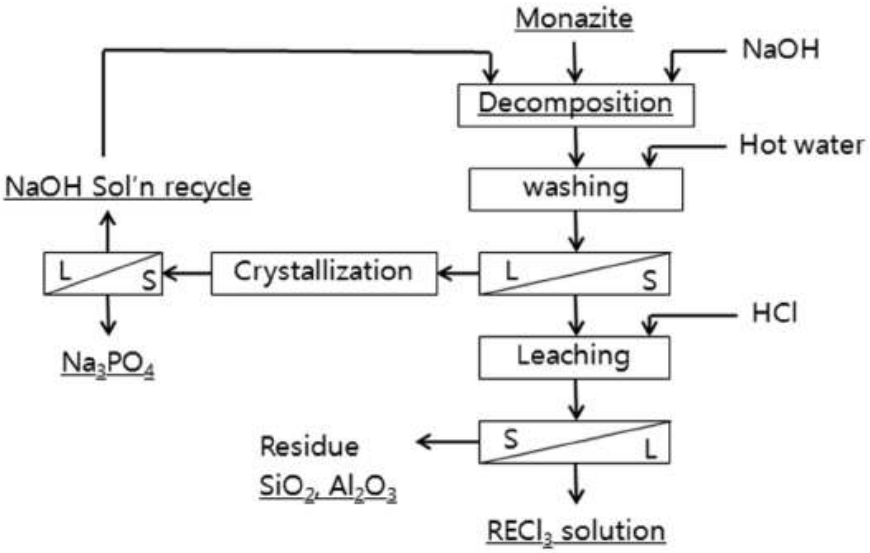

Figure 6. Decomposition and leaching process of monazite (Park et al., 2012)

$$REPO_4 + 3NaOH \rightarrow RE(OH)_3 + Na_3PO_4 \quad (6)$$

$$Th_3(PO_4)_4 + 12NaOH \rightarrow 3Th(OH)_4 + 4Na_3PO_4 \quad (7)$$

$$RE(OH)_3 + 3HCl \rightarrow RECl_3 + 3H_2O \quad (8)$$

2.3.2. Bastnasite[19]

Bastnasite can be leached in two methods: hydrochloric acid leaching and sulfuric acid leaching. Bastnasite leaching with HCl is conducted at 90 ℃ (Eq. (9)).

$$RE_2(CO_3)_3F_3 + 9HCl \rightarrow RECl_3(solution) + REF_3(solid) + 3HCl + 3H_2O + 3CO_2 \quad (9)$$

After Eq. (9), REF_3 solids are reacted with 20 % NaOH, which produce REE hydroxides (Eq. (10)). These hydroxides are used to neutralize excess HCl from Eq. (9) through the reaction shown in Eq. (11).

$$REF_3 + 3NaOH \rightarrow RE(OH)_3 + 3NaF\uparrow \quad (10)$$

$$RE(OH)_3 + 3HCl \rightarrow RECl_3 + 3H_2O \quad (11)$$

When bastnasite is leached with HCl, there are many advantages: low acid consumption, low cost, and a high level of REE recovery. However, the highly concentrated HCl can corrode facilities.

As shown in Figure 7, when using sulfuric acid, the ore has to be oxidized and then leached with sulfuric acid. Bastnasite can be leached effectively with sulfuric acid once the ore is roasted (Eq. (12)). Through the roasting, Ce is oxidized from +3 to +4 valance state and Ce separation from other elements is possible using this property.

$$RE_2O_3 + 2REF_3 + 6H_2SO_4 \rightarrow 2RE_2(SO_4)_3 + 6HF + 3H_2O \quad (12)$$

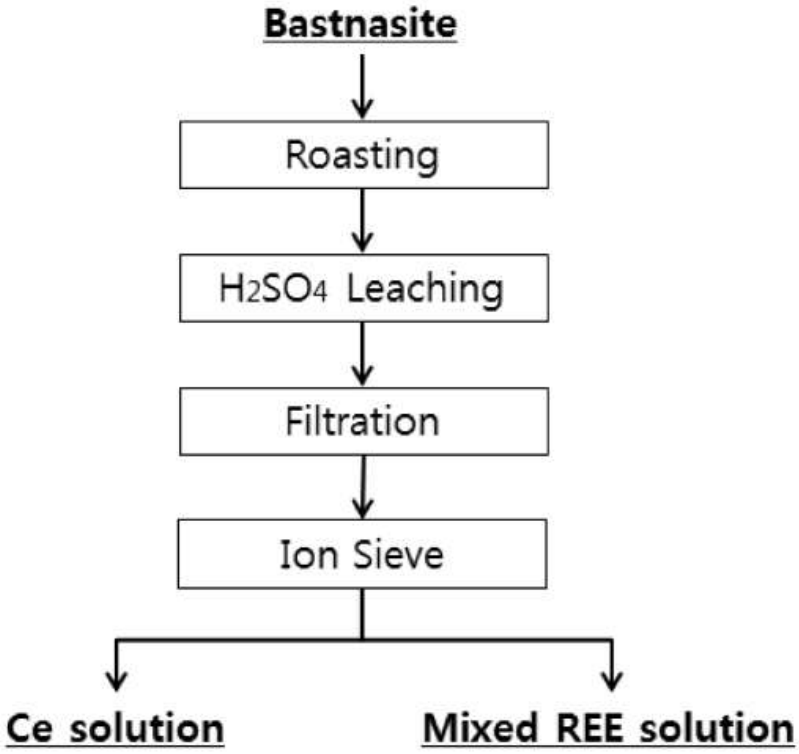

Figure 7. Sulfuric acid leaching process of bastnasite (Park et al., 2012)

2.3.3. Apatite[7]

REE in the Earth's crust is 0.015 % and in phosphate rock it can be as high as 1 % (Habashi, 1985). In contrast to igneous rocks, REE in phosphorites do not form their own minerals but enter into the crystal lattice of calcium phosphate in isomorphous substitutions for Ca^{2+}.

Sulfuric, nitric, and hydrochloric acids have been used as leaching reagents to extract REE from apatite (Esmaeil Jorjani et al., 2011). The recovery of REE and leaching product types vary depending on the leaching reagent.

When apatite is leached with sulfuric acid to obtain phosphoric acid, most of REE are lost to gypsum according to Eq. (13).

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF \quad (13)$$

REE in gypsum are present by isomorphous substitution with Ca^{2+}. The losses, amounting to about 70 %, can be minimized if the leaching is conducted at low temperatures with less concentrated H_2SO_4 (Habashi, 1985). Through leaching with nitric acid, REE can be recovered from gypsum. Figure 8 shows the flow sheet of REE recovery from wet process phosphoric acid by crystallization.

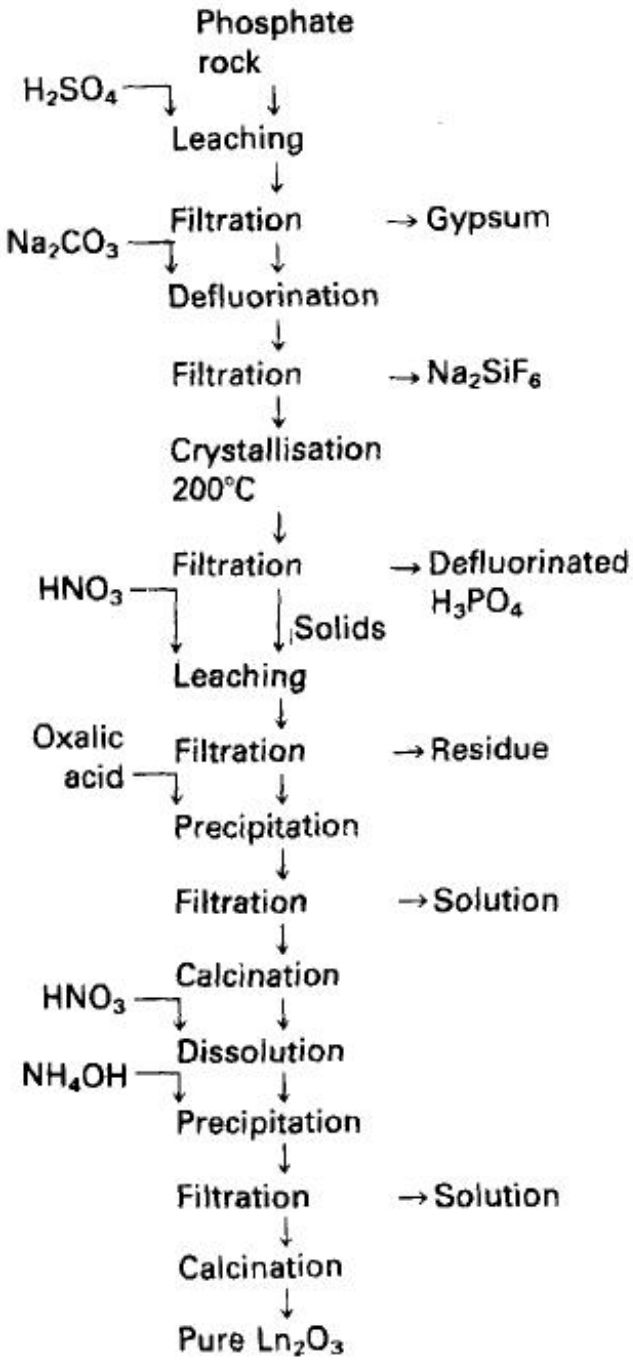

Figure 8. Recovery of pure REE oxides from wet process phosphoric acid by crystallization (Habashi, 1985)

When apatite is leached with nitric acid, all of REE are dissolved well. Thus, most of REE can be recovered from the ore. Apatite is easily leached at 60 ℃, using 50 ~ 60 % of nitric acid by Eq. (14).

$$Ca_{10}(PO_4)_6F_2 + 20HNO_3 \rightarrow 6H_3PO_4 + 10Ca(NO_3)_2 + 2HF \quad (14)$$

After filtering to remove silica, the filtrate is cooled to −5 °C to crystallize about 70 % of the $Ca(NO_3)_2 \cdot 4H_2O$ which is separated by centrifuging. The solution is defluorinated at times by adding sodium nitrate.

Next process can be done in two ways: crystallization and REE precipitation. In crystallization, the solution is crystallized into REE phosphates at an elevated temperature by neutralizing the solution using NH_4OH and heating it at 200 ℃ for an hour to make REE phosphate crystal.

REE precipitation by adjusting pH is when the solution is adjusted to 0.3 ~ 1.4 at temperatures of 70 ~ 90 ℃. The REE phosphate can be obtained and purified through the oxalate method or solvent extraction. Figure 9 shows the REE recovery by crystallization or precipitation.

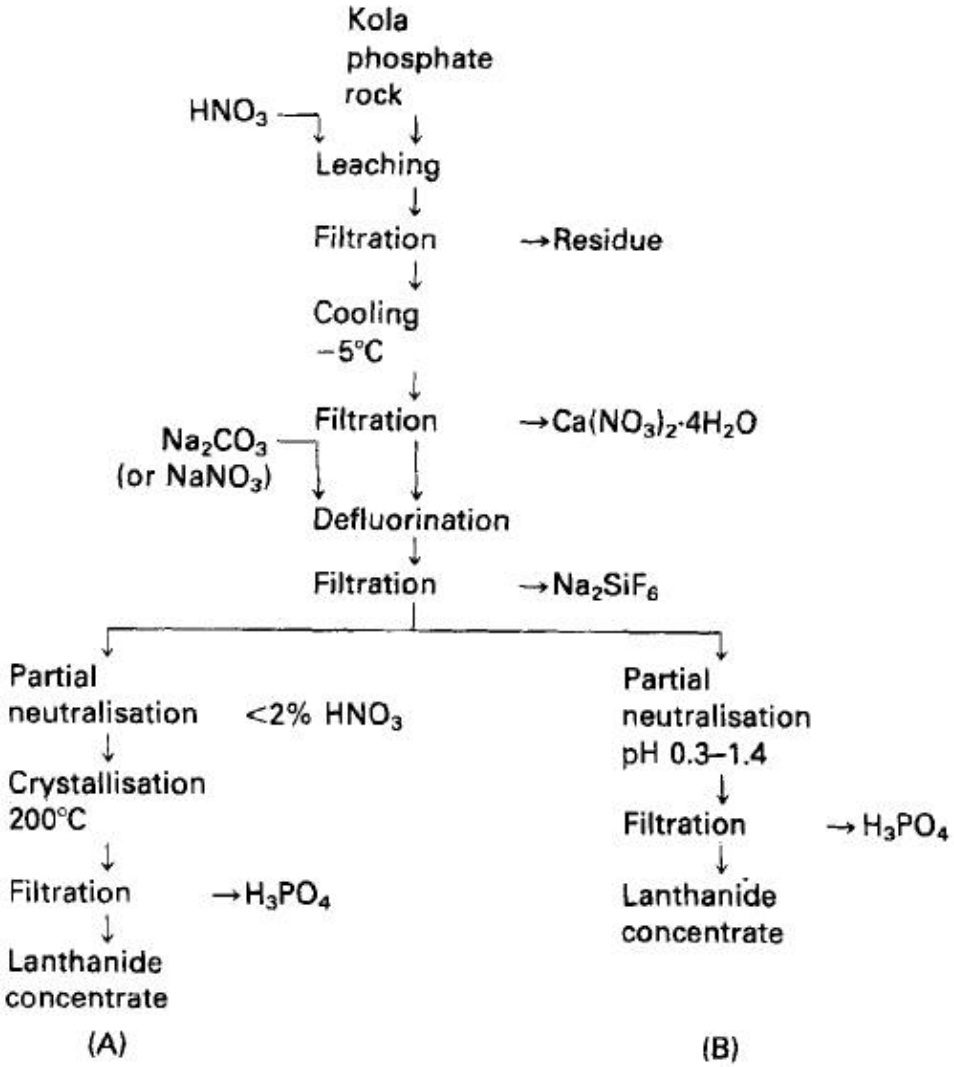

Figure 9. Recovery of REE from Kola phosphate by crystallization (A) or precipitation (B) (Habashi, 1985)

When apatite is leached with hydrochloric acid, the REE will be found in the solution. They can be isolated by precipitation as phosphate with $Ca(OH)_2$ to pH 1.5 ~ 1.6. The separated phosphate is redissolved with HCl and re-precipitated with oxalic acid. Then, REE oxalate is calcined at 800 ℃ and REE oxide containing 90 % REE is recovered as shown in Figure 10.

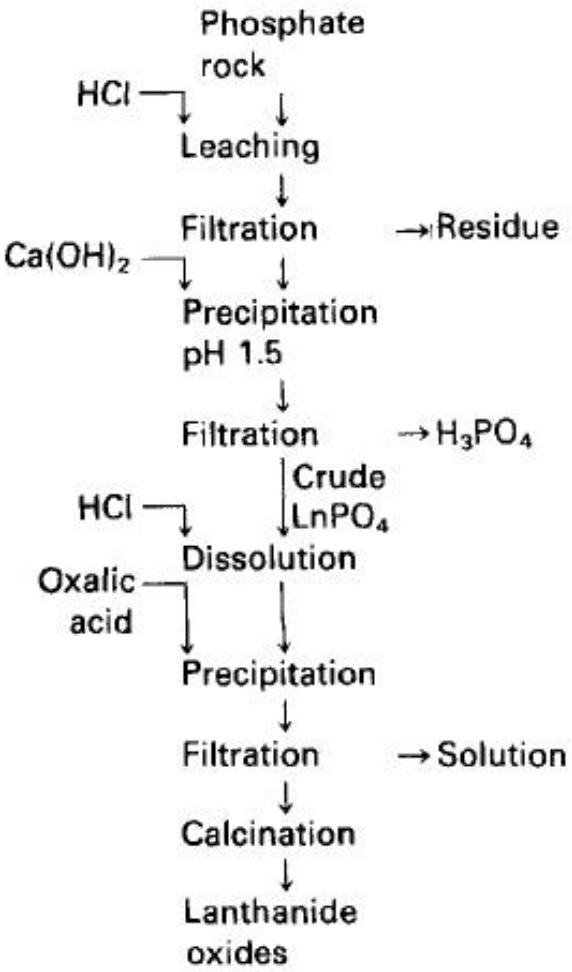

Figure 10. Recovery of REE from phosphate rock by HCl leaching process (Habashi, 1985)

3. Materials and methods

3.1. Sample characteristic

As shown in Figure 11, the Mushgai Khudag REE deposit is located in Mandal-Oboo, Omnogovi, Mongolia: 44° 21' 28'' ~ 44° 24' 08'' north latitude, 103° 29' 07'' ~ 104° 03' 09'' east longitude (Yoo et al., 2011).

The Mushgai Khudag REE deposit in southern Mongolia is composed of sheet-like magnetite-apatite ore bodies along the Jurassic syenite porphyry and host Paleozoic sedimentary rocks. The magnetite-apatite ores consist mainly of apatite, barian celestite, magnetite, hematite goethite, fluorite, gypsum, phlogopite, carbonates (mostly calcite), pyrite and monazite-(Ce) (Sanematsu et al., 2010).

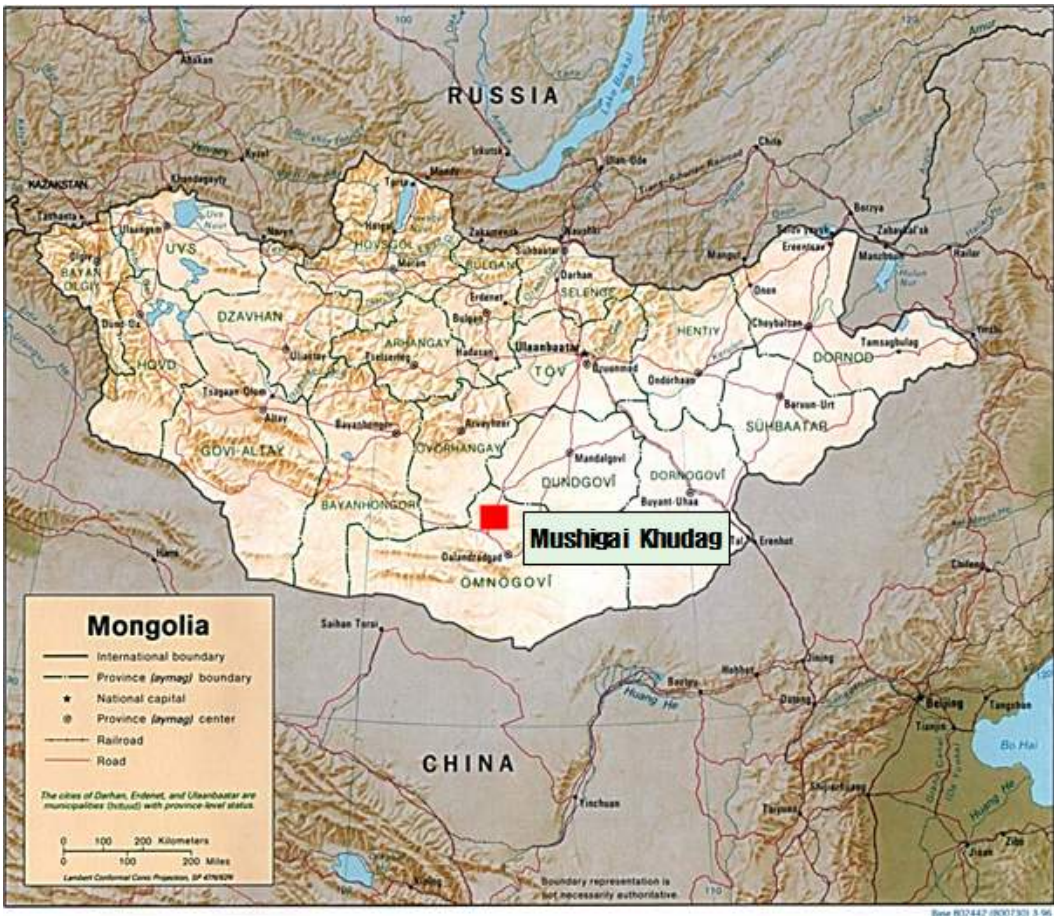

Figure 11. Location of Mushgai Khudag, in Mongolia (KORES, 2011)

The sample was collected from the High Grade Zone (HGZ) Mushgai Khudag area in Mongolia (Figure 12). A mineral analysis revealed that the main REE-bearing minerals are apatite (Figure 13) with small amounts of monazite and xenotime.

A chemical analysis of the sample is shown in Table 6, which shows total REE content at about 10 % of LREE with Ce being the most abundant element followed by La, Nd, Pr, and Y.

Figure 12. Sampling in HGZ

Figure 13. Apatite sample

Table 6. Chemical contents of HGZ sample

Formula	wt.%	Formula	wt.%
CaO	32.75	MgO	0.53
Fe_2O_3	22.91	SrO	0.47
P_2O_5	18.3	Na_2O	0.45
SiO_2	9.65	Pr_6O_{11}	0.42
CeO_2	5.8	MnO	0.29
La_2O_3	3.01	Y_2O_3	0.28
SO_3	1.8	K_2O	0.25
Nd_2O_3	1.48	ThO_2	0.06
Al_2O_3	0.87	ZnO	0.05
TiO_2	0.62	CuO	0.04

The sample was crushed to -1 mm in stages by a jaw crusher and disk mill. It was then ground by ball mill or centrifugal mill to prepare three different sizes: (1) 90 % passing 50 mesh (0.3 mm), (2) 90 % passing 100 mesh (0.15 mm), and (3) 85 % passing 200 mesh (0.075 mm). The complete size distributions are shown in Tables 7 ~ 9 and Figures 14 ~ 16.

Table 7. Size analysis of HGZ sample (d_{90}: 50 mesh)

Mesh	Size (mm)	Wt. (g)	Cumulative wt. (g)	Cumulative % passing
16	1.18	0.04	34.53	100
20	0.85	0.21	34.49	99.9
30	0.6	0.64	34.28	99.3
40	0.425	2.42	33.64	97.4
50	0.3	3.46	31.22	90.4
70	0.212	4.53	27.76	80.4
100	0.15	4.02	23.23	67.3
140	0.106	3.62	19.21	55.6
200	0.075	3.7	15.59	45.1
270	0.053033	3.86	11.89	34.4
400	0.0375	8.03	8.03	23.3
	Total	34.53		

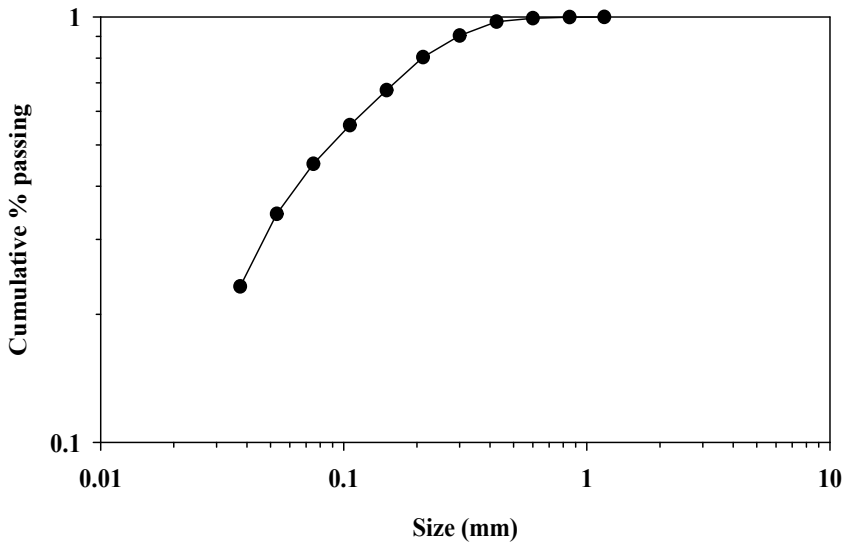

Figure 14. Cumulative size distribution of HGZ sample (d_{90}: 50 mesh)

Table 8. Size analysis of HGZ sample (d_{90}: 100 mesh)

Mesh	Size (mm)	Wt. (g)	Cumulative wt. (g)	Cumulative % passing
16	1.18	0	34.63	100
20	0.85	0	34.63	100
30	0.6	0	34.63	100
40	0.425	0.03	34.63	100
50	0.3	0.67	34.6	99.9
70	0.212	2.43	33.93	98.0
100	0.15	3.98	31.5	91.0
140	0.106	4.17	27.52	79.5
200	0.075	5.26	23.35	67.4
270	0.053033	7.61	18.09	52.2
400	0.0375	10.48	10.48	30.3
Total		34.63		

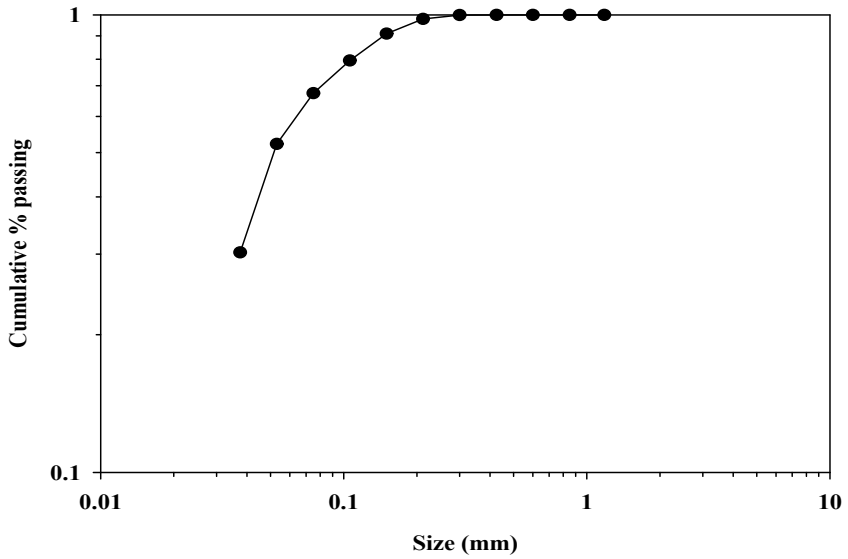

Figure 15. Cumulative size distribution of HGZ sample (d_{90}: 100 mesh)

Table 9. Size analysis of HGZ sample (d_{85}: 200 mesh)

Size (mm)	Cumulative %passing
0.631	100
0.417	100
0.316	99.9
0.209	99.1
0.158	97.6
0.105	92.6
0.079	87.0
0.0525	75.8
0.0347	63.6
0.0263	55.5
0.0174	44.3
0.0132	37.5

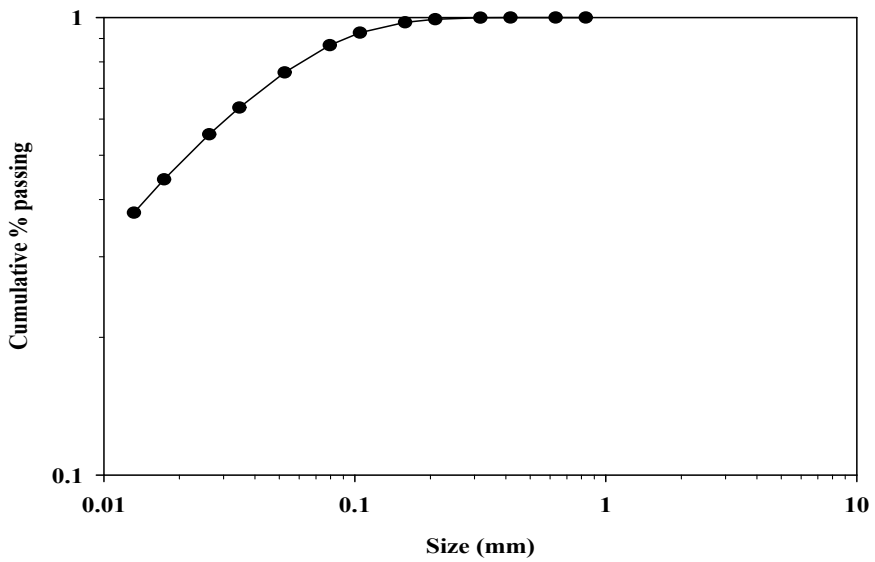

Figure 16. Cumulative size distribution of HGZ sample (d_{85}: 200 mesh)

3.2. Experimental methods

3.2.1. Leaching experiment

Sulfuric, hydrochloric, and nitric acid at various concentrations (0.1 ~ 13.0 M for sulfuric acid, 0.6 ~ 3.85 M for hydrochloric acid, and 1.0 ~ 5.5 M for nitric acid) were used as leaching reagents for leaching experiments. The pH of the acid solution was measured and when the pH stabilized, the ore sample was added to a 600 mL beaker containing the acid solution. When testing at increased temperatures, the sample was added to a double-walled glass vessel after the temperature reached the target point. The solution temperature was maintained by circulating hot water and the slurry was then agitated with an impeller-type stirrer at 300 rpm. Solution samples were collected at regular intervals and filtered using 0.45 ㎛ cellulose acetate filter. The filtrate was diluted 10 times with 1.0 M HCl and subjected to ICP analysis. Leaching tests were conducted at three different temperatures: 25 ℃, 50 ℃, and 80 ℃ to investigate the temperature effect on leaching.

3.2.2. Magnetic separation

To remove Fe, wet magnetic separation was performed using a laboratory magnetic separator (ERIEZ, Wet high intensity magnetic separator L-4). 10 g of the sample and 0.01 g of aerosol-OT was added to a 2 L beaker containing 90 mL of water. The slurry was mixed by hand-shaking and was put into the magnetic separator with an applied magnetic field at various magnetic intensities: 1000 gauss, 4000 gauss, and 12000 gauss. The beaker and the separator were washed with ample water and then some slurry was recovered as the non-magnetic portion.

After removing the magnetic field, the separator was washed again and the remaining slurry was recovered as the magnetic portion. The separated product was dried in the oven at 110 ℃ for 12 hours, weighed, and recovered.

3.2.3. Nitro-hydrochloric acid digestion - the sample concentration measurement

After the leaching experiment was completed, the residue was separated from leachate. The concentration of leachate, and raw sample and residue digested using nitro-hydrochloric acid were analyzed through Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

The nitro-hydrochloric acid digestion was prepared by adding 4 mL of acid to 0.25 g of each sample. The digestion was progressed at 70 ℃ for an hour until the acid slurry was filtered using 0.45 ㎛ cellulose acetate filter. Distilled water was added to filtrate to make 10 mL.

4. Results and discussion

4.1. Leaching kinetics

To determine the optimum leaching time for the HGZ sample, leaching levels were evaluated at various leaching times. 13.0 M sulfuric acid, 2.0 M hydrochloric and nitric acid were used as leaching reagents and Tables 10 ~ 12 show the detailed leaching conditions. The leaching kinetics were very fast for all REE with less than 1 hr to reach maximum leaching levels.

Figure 17 shows the typical results when 13.0 M sulfuric acid was used and the leaching levels decreased after 3 hrs. This is probably due to the precipitation of REE with SO_4^{2-} as discussed in detail in the next section.

Table 10. Experiment conditions of leaching kinetics (1)

Content	Condition
Acid type	Sulfuric acid
Acid concentration	13.0 M
Pulp density	10 % (sample 10 g, acid solution 90 mL)
Sample size	d_{90}: 50 mesh (0.3 mm)
Residence time	5 hrs
Agitation speed	300 rpm
Temperature	room temperature (25 ℃)

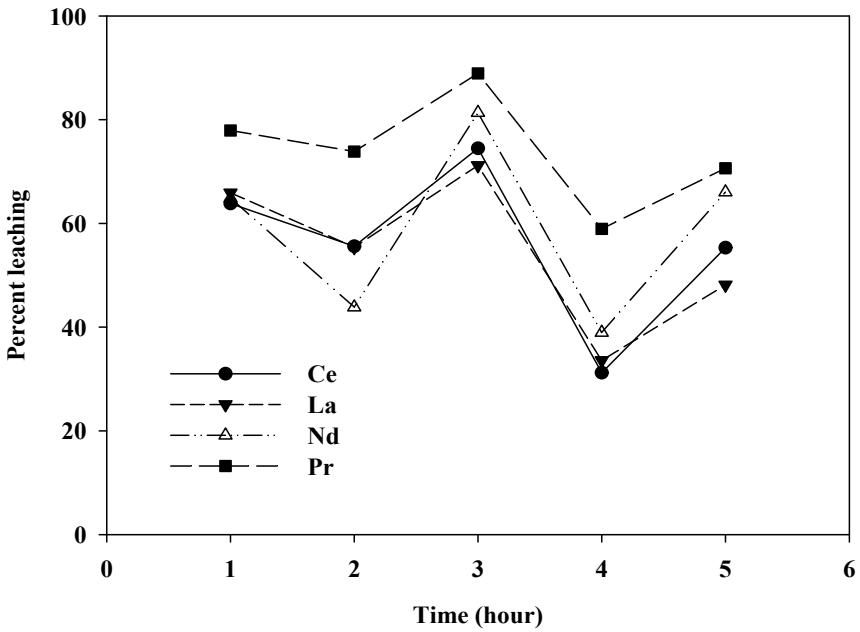

Figure 17. Change of leaching levels with time (leaching reagent: 13.0 M sulfuric acid)

Figure 18 shows that leaching levels change with time when 2.0 M of hydrochloric acid was used as a leaching reagent. 90 % REE were leached out in 10 minutes, and after 1 hr, almost 100 % REE were leached. Unfortunately, radioactive elements U and Th were leached out together with REE, indicating that radioactive elements removal from the leachate may be necessary by using separation techniques such as selective precipitation or solvent extraction method.

Table 11. Experiment conditions of leaching kinetics (2)

Content	Condition
Acid type	Hydrochloric acid
Acid concentration	2.0 M
Pulp density	10 % (sample 10 g, acid solution 90 mL)
Sample size	d_{90}: 50 mesh (0.3 mm)
Residence time	2 hrs
Agitation speed	300 rpm
Temperature	room temperature (25 ℃)

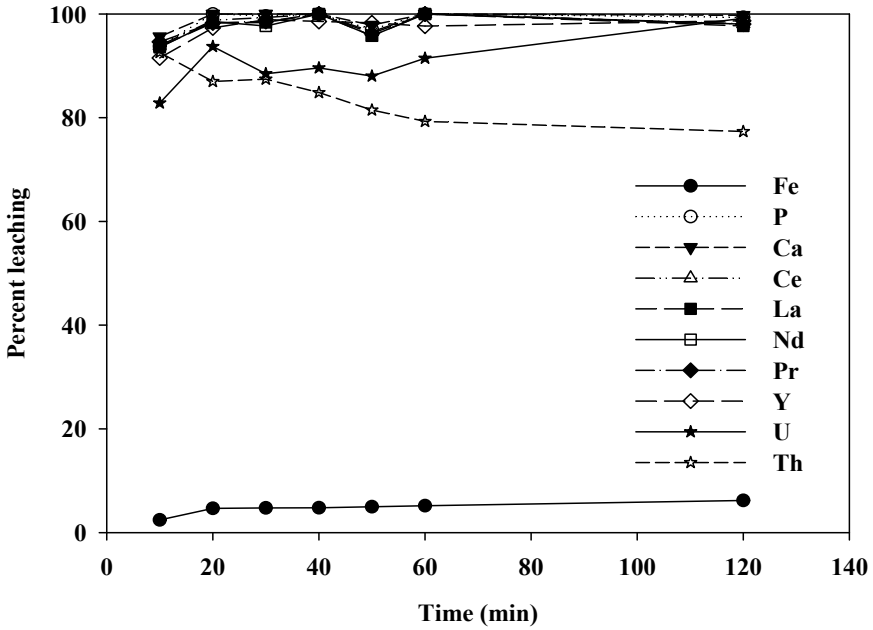

Figure 18. Change of leaching levels with time (leaching reagent: 2.0 M hydrochloric acid)

When nitric acid was used as the leaching reagent, leaching levels were high like with hydrochloric acid. As shown in Figure 19, 80 ~ 90 % REE were leached out in 30 minutes, and leaching levels reached 100 % at 3 hrs. There are also high levels of impurities.

Table 12. Experiment conditions of leaching kinetics (3)

Content	Condition
Acid type	Nitric acid
Acid concentration	2.0 M
Pulp density	10 % (sample 10 g, acid solution 90 mL)
Sample size	d_{90}: 50 mesh (0.3 mm)
Residence time	3 hrs
Agitation speed	300 rpm
Temperature	room temperature (25 ℃)

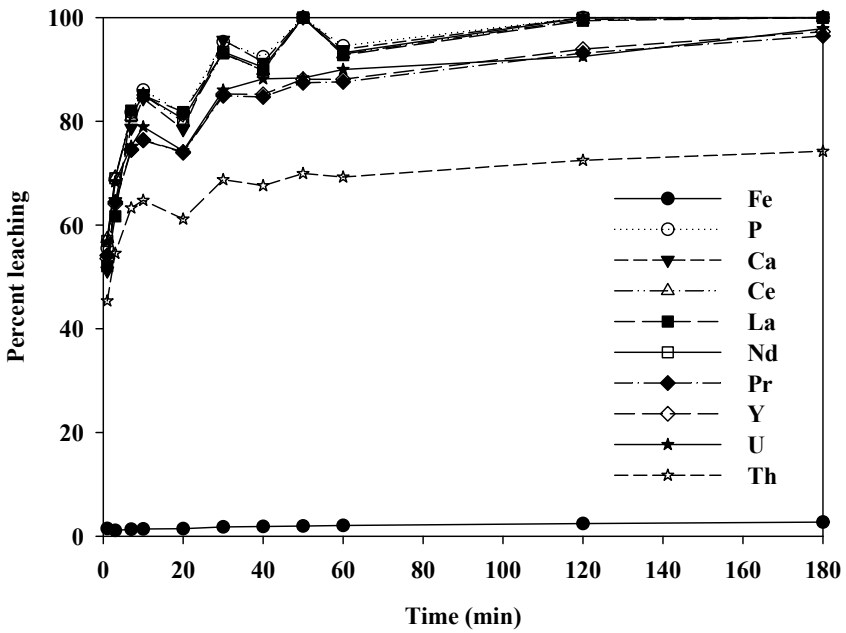

Figure 19. Change of leaching levels with time (leaching reagent: 2.0 M nitric acid)

4.2. Effect of acid concentration and type on leaching levels

To dissolve target materials in the ore, a suitable acid concentration must be maintained. At low acid concentration, materials cannot be dissolved adequately. On the contrary, various impurities can be leached with target materials at high acid concentration, which can cause deleterious effects. Thus, before leaching, the optimum leaching pH has to be determined with thermodynamic data.

Leaching experiments were performed at various acid concentrations to find optimum acid concentrations for leaching REE in the ore. Additionally, changes in leaching efficiency was studied using sulfuric, hydrochloric, and nitric acid as leaching reagents to determine the optimum leaching reagent.

Figure 20 shows the changes in leaching efficiency at 25 ℃ for various sulfuric acid concentrations and the experimental conditions are listed in Table 13. When the acid concentration was less than 5.0 M, the leaching levels were below 50 %. The leaching level increased with increased sulfuric acid, but did not go beyond 80 % even at 13.0 M of sulfuric acid. As discussed previously, this may be from the co-precipitation of REE during calcium sulfate formation (Habashi, 1985). The XRD analysis of the residue shows the presence of $CaSO_4$ (Figure 21). Therefore, sulfuric acid may not be suitable for this ore as leaching is limited due to formation of sulfates.

Table 13. Experiment conditions of effect of acid concentration (1)

Content	Condition
Acid type	Sulfuric acid
Acid concentration	0.1 M, 1.0 M, 2.0 M, 5.0 M, 9.0 M, 13.0 M
Pulp density	10 % (sample 10 g, acid solution 90 mL)
Sample size	d_{90}: 50 mesh (0.3 mm)
Residence time	5 hrs
Agitation speed	300 rpm
Temperature	room temperature (25 ℃)

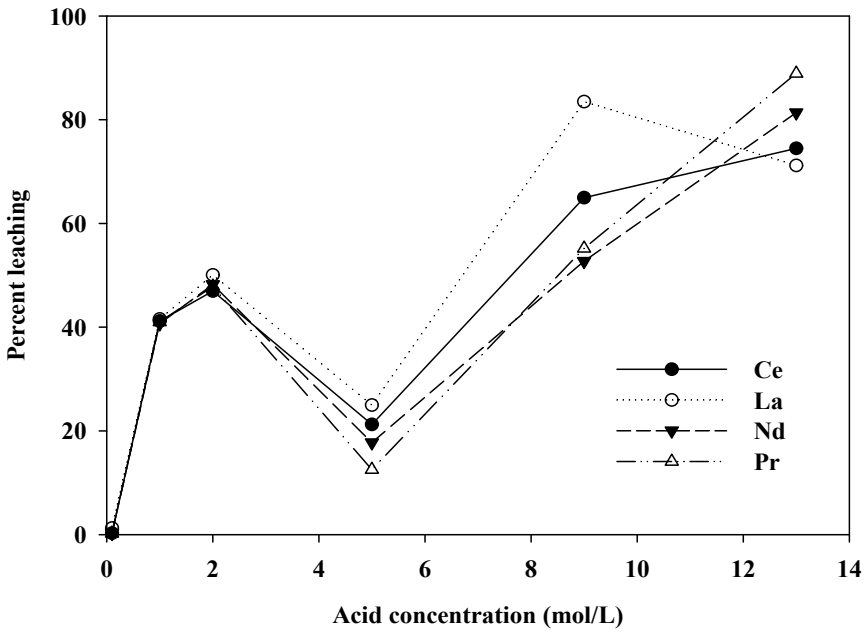

Figure 20. Change of leaching levels at various sulfuric acid concentrations

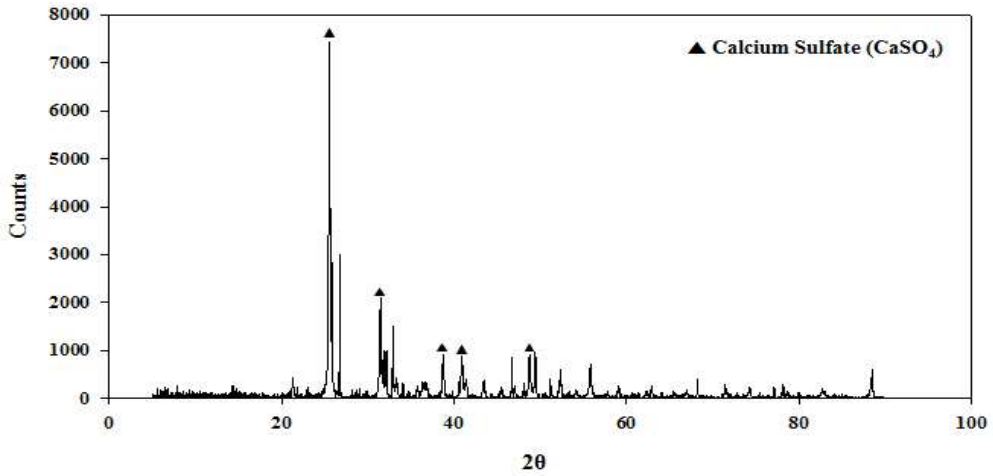

Figure 21. Result of XRD analysis about residue from leaching with 13.0 M of sulfuric acid

Figure 22 shows the change in leaching levels at different concentrations of hydrochloric acid with the leaching conditions shown in Table 14. None of the REE was leached out when the acid concentration was less than 1.0 M, but at higher concentrations of hydrochloric acid, the leaching levels started to increase sharply and reach 97 ~ 98 % at 2.0 M. At acid concentration of 2.75 M, nearly 100 % REE were leached out. However, the concentrations of Fe and Ca ions in the leachate were found to be very high (Fe: 260 ppm, Ca: 28000 ppm), which can increase the level of impurities when the REE is recovered as oxalate or carbonate precipitates from REE chloride solution.

Table 14. Experiment conditions of effect of acid concentration (2)

Content	Condition
Acid type	Hydrochloric acid
Acid concentration	0.6 M, 1.0 M, 1.5 M, 2.0 M, 2.4 M, 2.75 M, 3.85 M
Pulp density	10 % (sample 10 g, acid solution 90 mL)
Sample size	d_{90}: 50 mesh (0.3 mm)
Residence time	5 hrs
Agitation speed	300 rpm
Temperature	room temperature (25 ℃)

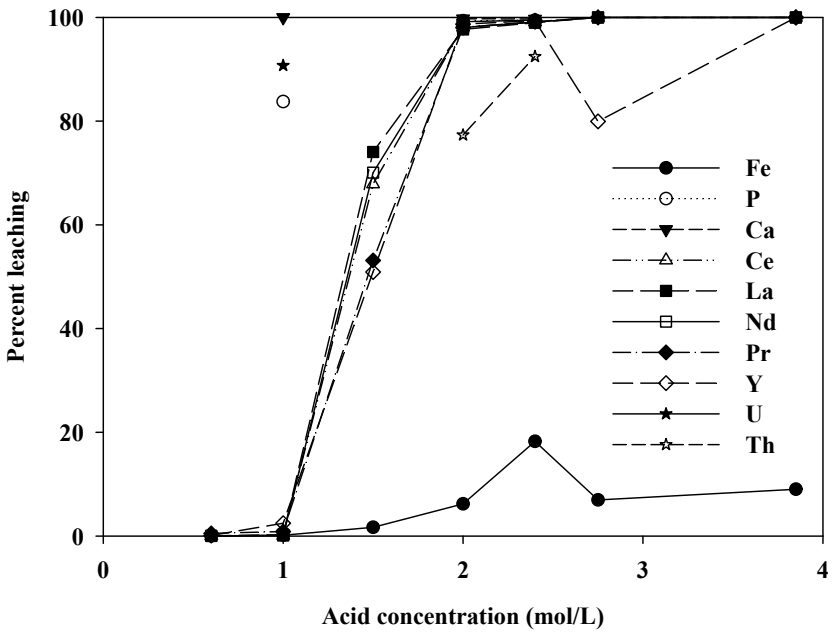

Figure 22. Change of leaching levels at various hydrochloric acid concentrations

The leaching experiments when nitric acid was used are shown in Figure 23 while Table 15 shows detailed leaching conditions. The results are similar for hydrochloric acid. REE were not leached at 1.0 M, but leaching levels were increased dramatically to about 100 % at 2.0 M. However, many impurities were leached out, which means they must be removed. Furthermore, nitric acid is more expensive than hydrochloric acid, which may not be viable for economical processes.

Table 15. Experiment conditions of effect of acid concentration (3)

Content	Condition
Acid type	Nitric acid
Acid concentration	1.0 M, 2.0 M, 5.5 M
Pulp density	10 % (sample 10 g, acid solution 90 mL)
Sample size	d_{90}: 50 mesh (0.3 mm)
Residence time	5 hrs
Agitation speed	300 rpm
Temperature	room temperature (25 ℃)

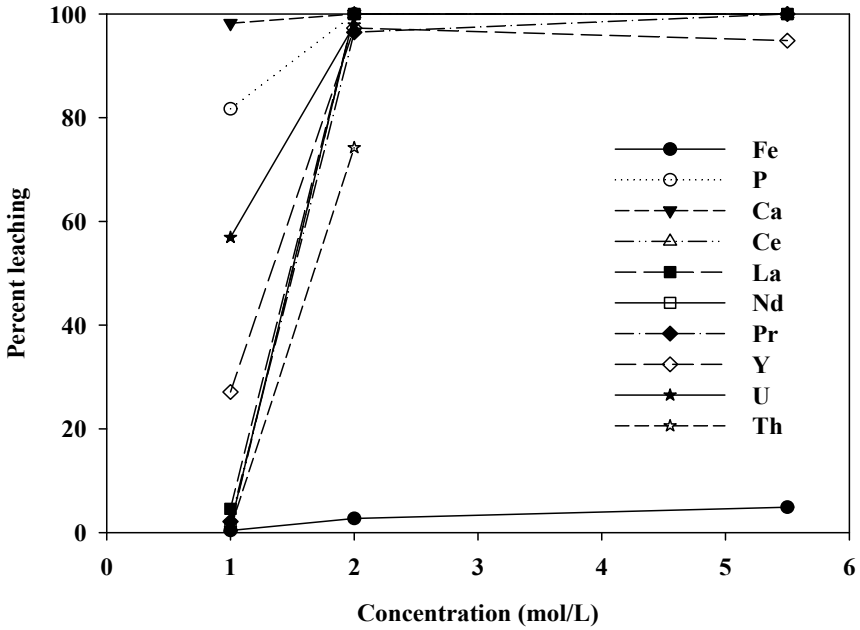

Figure 23. Change of leaching levels at various nitric acid concentrations

4.3. Effect of temperature on leaching levels

Generally, the chemical reaction rate is faster at a higher temperature. The leaching reaction is also one of the chemical reactions, thus the leaching levels may increase at elevated temperatures. The leaching tests were conducted at elevated temperatures.

To determine the effect temperature has on the reaction, leaching experiments were performed using 13.0 M sulfuric acid at room temperature (25 ℃) and 80 ℃. The leaching time was 3 hours at 80 ℃ with detailed experimental conditions given in Table 16 and results in Figure 24.

Table 16. Experiment conditions of effect of temperature (1)

Content	Condition
Acid type	Sulfuric acid
Acid concentration	13.0 M
Pulp density	10 % (sample 10 g, acid solution 90 mL)
Sample size	d_{90}: 50 mesh (0.3 mm)
Residence time	3 hrs
Agitation speed	300 rpm
Temperature	25 ℃, 80 ℃

When the temperature was increased to 80 ℃, the leaching levels of most REE increased significantly up to over 80 %. However, the same leaching levels can be obtained with hydrochloric acid under much milder conditions. Therefore, hydrochloric acid is a better choice as a leaching reagent for this ore.

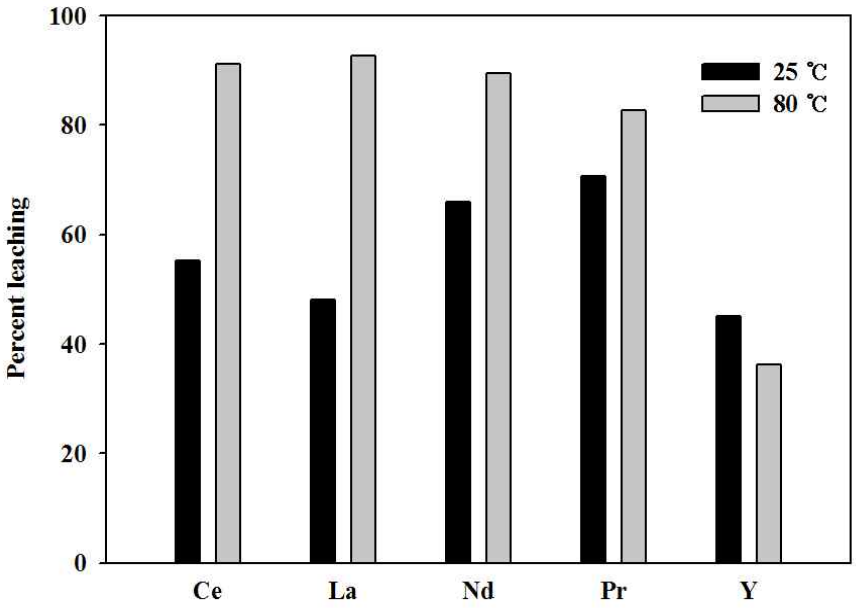

Figure 24. Comparison of leaching using 13.0 M sulfuric acid at 25 ℃ and 80 ℃

Leaching experiments were performed at some temperatures using hydrochloric acid as the leaching reagent with leaching conditions listed in Table 17. Since almost 100 % REE were leached out with 2.0 M hydrochloric acid, tests were conducted using 1.0 M hydrochloric acid at 25 ℃, 50 ℃, and 80 ℃.

Table 17. Experiment conditions of effect of temperature (2)

Content	Condition
Acid type	Hydrochloric acid
Acid concentration	1.0 M
Pulp density	10 % (sample 10 g, acid solution 90 mL)
Sample size	d_{90}: 50 mesh (0.3 mm)
Residence time	3 hrs
Agitation speed	300 rpm
Temperature	25 ℃, 50 ℃, 80 ℃

As shown in Figure 25, there was not much increase in the leaching levels for REE, but other impurity ions (Fe, P, Ca, U) were leached out as the temperature increased. Therefore, there was no benefit to operating at higher temperatures and it is better to operate at higher concentrations of hydrochloric acid than to operate at elevated temperatures with a lower acid concentration.

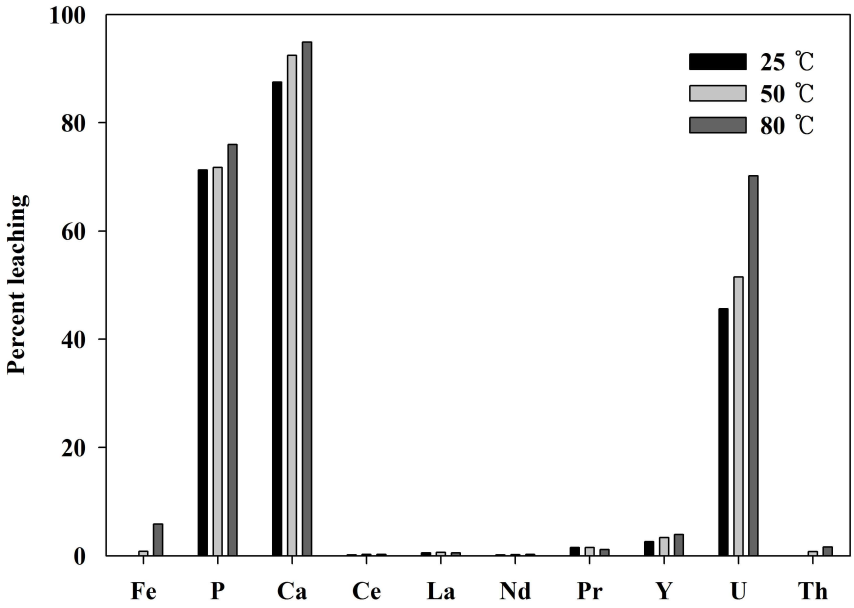

Figure 25. Comparison of leaching using 1.0 M hydrochloric acid at 25 ℃, 50 ℃, and 80 ℃

4.4. Effect of magnetic separation

The sample contained a large amount of Fe. From the chemical analysis of the ore, the concentration of Fe_2O_3 is a very high 23 %. Therefore, steps were taken to try to remove iron bearing minerals from the sample prior to leaching.

Table 18 shows the chemical analysis of the sample before and after magnetic separation at three different magnetic intensities. At 1000 gauss, the Fe_2O_3 concentration of the non-magnetic portion decreased significantly to about 6.5 % from the feed value of 22.9 %. The REE contents were increased in a corresponding degree as REE containing apatite is non-magnetic. Some REE were lost to the magnetic stream, but the REE recovery to the non-magnetic stream was over 90 %. In particular, all Pr and Y were recovered in the non-magnetic portion.

At 4000 gauss, the Fe recovery to the non-magnetic portion was greatly decreased to about 5 %. However, more REE loss occurred, reducing REE recovery to 80 % as well as Pr and Y recovered 100 % in the non-magnetic portion.

At 12000 gauss, the concentration of Fe in the non-magnetic portion was just 0.95 % and recovery also decreased to 3 %. However, the recovery of all REE including Pr and Y decreased significantly to around 50 %.

Therefore, the non-magnetic portion at 1000 gauss was used for leaching experiments because Fe was removed from

the sample significantly, and REE content was high. The Fe_2O_3 content of the magnetic stream was very high, which could point to iron ore concentrate that can be sold to iron smelters.

Table 18. Fe and REE contents of raw sample and magnetic separated samples

Magnetic intensity	Sample	Yield (%)	Fe_2O_3	CeO_2	La_2O_3	Nd_2O_3	Pr_6O_{11}	Y_2O_3
-	Raw	100.0	22.91	5.80	3.01	1.48	0.42	0.28
1000 gauss	Magnetic	19.56	65.17	2.14	1.22	0.53	0.00	0.00
	Non-mag.	80.44	6.47	7.29	3.83	1.91	0.58	0.28
Recovery to Non-mag (%)			29.00	93.34	92.81	93.66	100.0	100.0
4000 gauss	Magnetic	31.86	52.68	2.99	1.60	0.77	0.00	0.00
	Non-mag.	68.14	1.46	7.60	4.00	2.03	0.60	0.30
Recovery to Non-mag (%)			5.60	84.46	84.24	85.00	100.0	100.0
12000 gauss	Magnetic	56.29	23.09	5.69	3.04	1.44	0.46	0.21
	Non-mag.	43.71	0.95	7.21	3.74	1.90	0.55	0.29
Recovery to Non-mag (%)			3.08	49.60	48.86	50.61	47.92	51.01

2.0 M hydrochloric acid was used for the leaching experiment of a magnetic separated sample. Table 19 shows the experimental conditions while the results are shown in Figures 26 and 27. The leaching levels of Fe were less than 10 %, using both raw samples and separated samples, but the Fe concentration in the leachate after magnetic separation was just 60 ppm as compared to 260 ppm without magnetic separation. The leaching levels of REE remained as high, so it is better to perform leaching after magnetic separation when removing Fe.

Table 19. Experiment conditions of leaching of magnetic separated sample

Content	Condition
Acid type	Hydrochloric acid
Acid concentration	2.0 M
Pulp density	10 % (sample 10 g, acid solution 90 mL)
Sample characteristic	d_{90}: 100 mesh (0.15 mm) magnetic separated at 1000 gauss
Residence time	1 hr
Agitation speed	300 rpm
Temperature	25 ℃

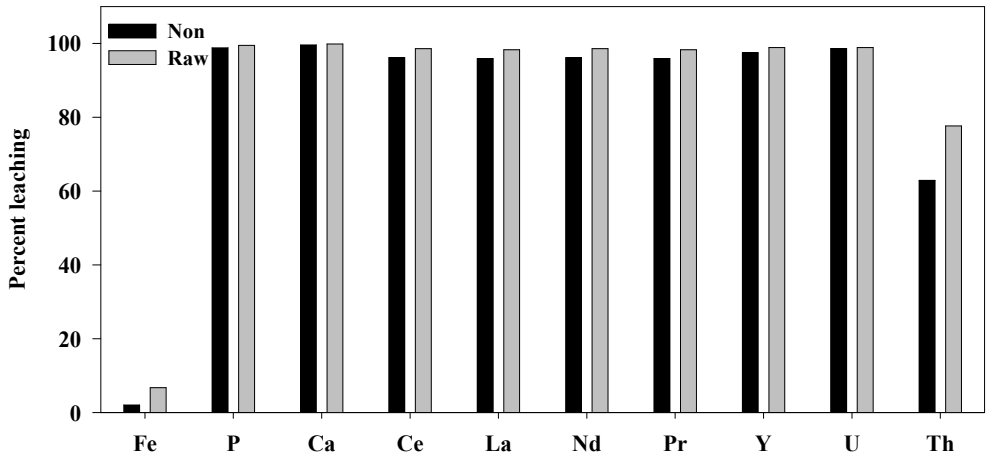

Figure 26. Comparison of leaching levels for REE of the raw sample and the magnetic separated sample

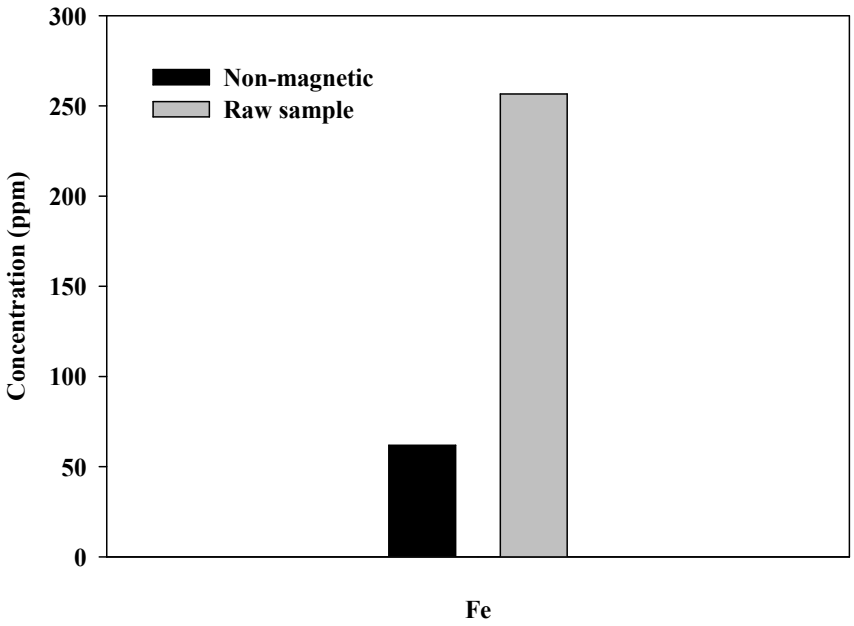

Figure 27. Concentration of Fe in the leachate of the raw sample and the magnetic separated sample

4.5. Effect of particle size

When materials are extracted from the ore, the particle size must be considered. The cost of mineral processing is greatly affected by comminution, because this step is energy intensive and can determine the liberation degree. If the particle size is too big, the liberation degree can be low and have a bad target material recovery. However, when the particle size is too small, gangue minerals can be extracted. Therefore, it is important to find the optimum particle size.

To study effects of particle size in a leaching experiment, 3 different particle sizes were used: (1) 90 % passing 50 mesh (0.3 mm), (2) 90 % passing 100 mesh (0.15 mm), and (3) 85 % passing 200 mesh (0.075 mm). Table 20 shows the detailed experimental conditions.

Table 20. Experiment conditions of effect of particle size

Content	Condition
Acid type	Hydrochloric acid
Acid concentration	2.0 M
Pulp density	10 % (sample 10 g, acid solution 90 mL)
Sample size	d_{90}: 50 mesh (0.3 mm) d_{90}: 100 mesh (0.15 mm) d_{85}: 200 mesh (0.075 mm)
Residence time	1 ~ 2 hrs
Agitation speed	300 rpm
Temperature	25 ℃

Each sample was leached for 1 or 2 hours with 2.0 M hydrochloric acid. Figure 28 shows that the leaching levels of REE are more than 90 % at all particle sizes and that there was no big difference in the leaching levels of REE with changes in particle size.

Each element concentration in leachate was compared in Figure 29 and showed that there were some differences in concentration of REE, Ca, and P, but no consistent variation with particle size. Therefore, the particle size of 90 % passing 50 mesh is fine enough to give leaching levels.

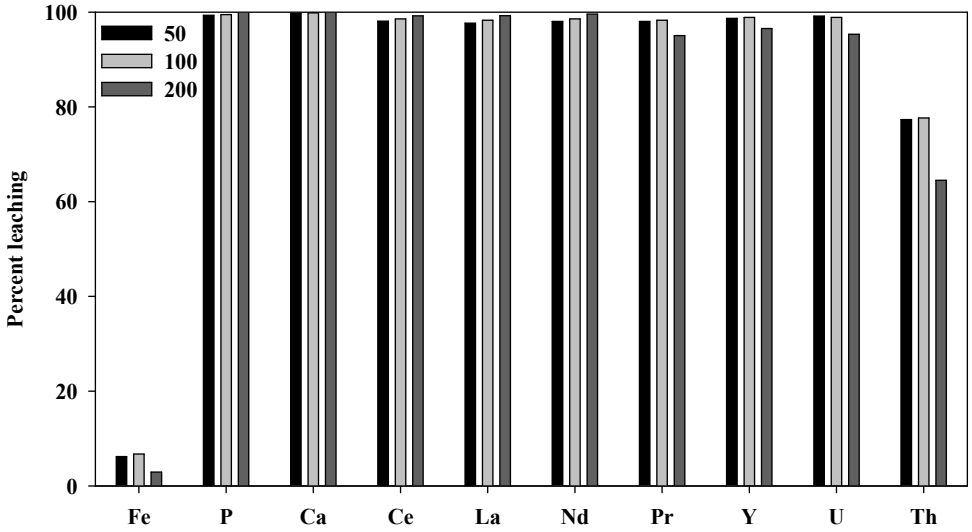

Figure 28. Comparison of leaching levels with change of sample particle size

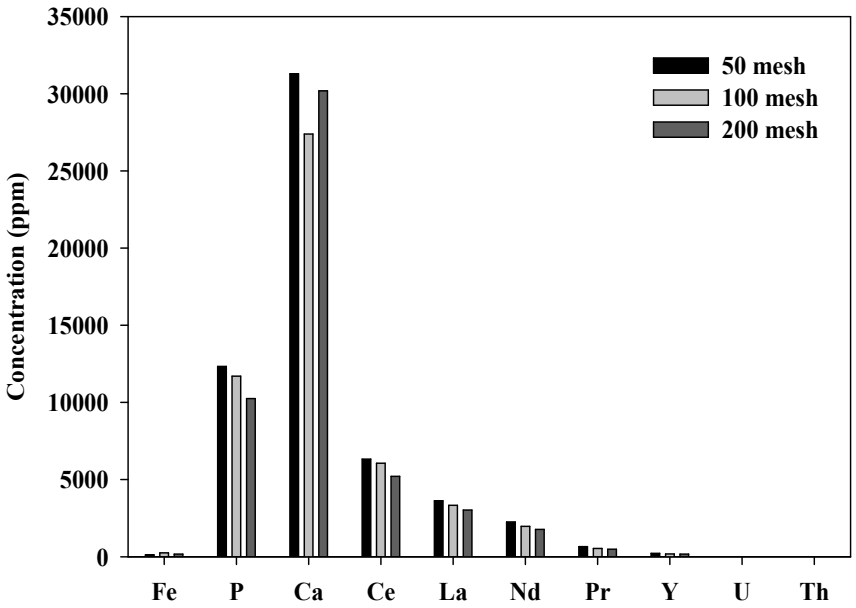

Figure 29. Comparison of concentration of elements in leachate with change of sample particle size

4.6. Effect of pulp density

Pulp density is another critical factor for determining leaching efficiency. If pulp density is lower, leaching levels are improved because the amount of solution is much greater than that of solids. At high solid concentrations, it becomes difficult to leach the ore because the amount of solids is too much. However, it may not be economical to operate at low solid concentrations because the consumption of leaching reagent is too high. Thus, it is imperative to find the optimum pulp density for economical reasons, and the experimental conditions are shown in Table 21.

Table 21. Experiment conditions of effect of pulp density

Content	Condition
Acid type	Hydrochloric acid
Acid concentration	2.0 M
Pulp density	10 %, 15 %, 25 %, 40 %
Sample size	d_{90}: 50 mesh (0.3 mm)
Residence time	2 ~ 5 hrs
Agitation speed	300 rpm
Temperature	25 ℃

As shown in Figure 30, at 10 % pulp density, almost 100 % REE were leached out in an hour, but the leaching levels of the impurities (Ca, P, Th, U) were more than 80 % for all except Fe.

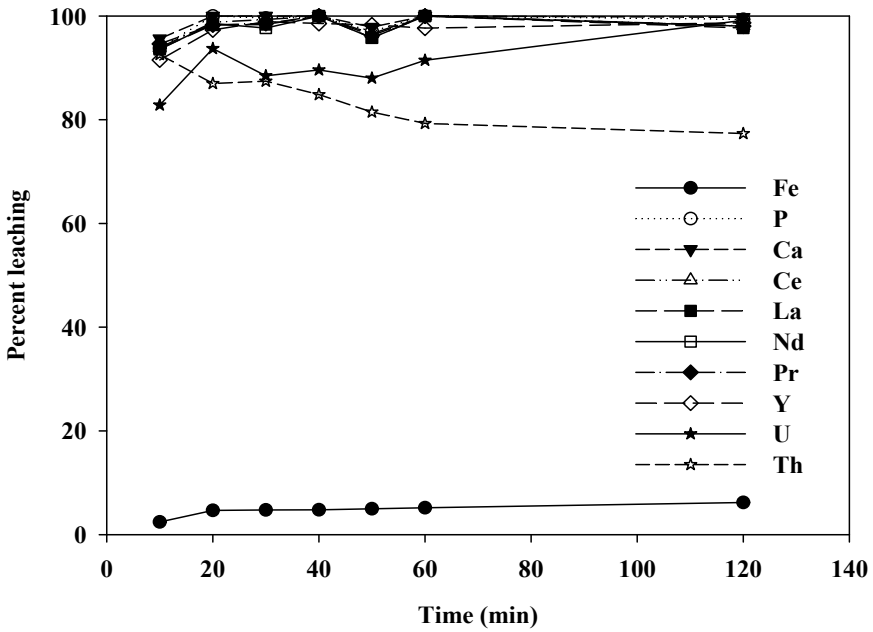

Figure 30. Change of leaching levels with time at 10 % of pulp density

At 15 %, the leaching kinetics changed significantly as shown in Figure 31. Leaching levels of most REE reached the maximum at around 20 minutes (above 80 % except Y, 77 %). However, leaching levels started to decrease to 30 ~ 50 % after 2 hrs. Therefore, the optimum leaching levels are expected to be reached in 30 minutes and impurities also need to be removed.

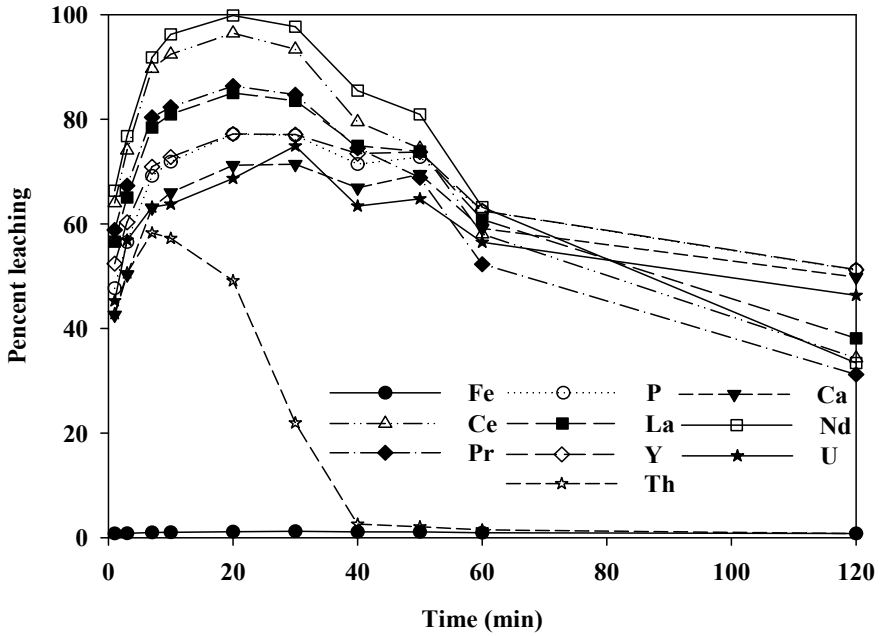

Figure 31. Change of leaching levels with time at 15 % of pulp density

Meanwhile, at 25 % pulp density, REE leaching levels were more than 80 % in 3 minutes, as shown in Figure 32. The leaching levels decreased sharply and approached 0 after 40 minutes. Thus, 25 % is not a suitable pulp density for REE recovery. However, the leaching levels of some impurities such as Ca, P, and U, remained high, which indicated that the impurity ions can be removed by solid-liquid separation. The solid residue is then subject to the second-stage leaching to recover REE at a proper pulp density.

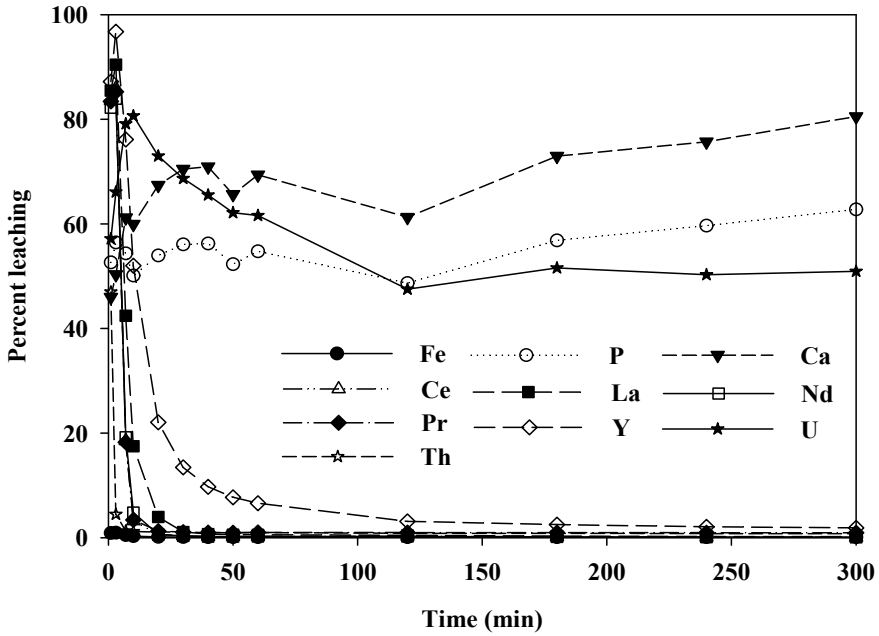

Figure 32. Change of leaching levels with time at 25 % of pulp density

At 40 % pulp density, REE leaching levels reached 30 ~ 40 % in just a few minute and decreased to 0 ~ 1 % after 20 minutes (Figure 33). Furthermore, impurity leaching levels were about 20 ~ 40 % compared to 50 ~ 80 % at 25 % solids concentration. Thus, pulp density at 40 % is not suitable in terms of both REE recovery and impurity removal potential.

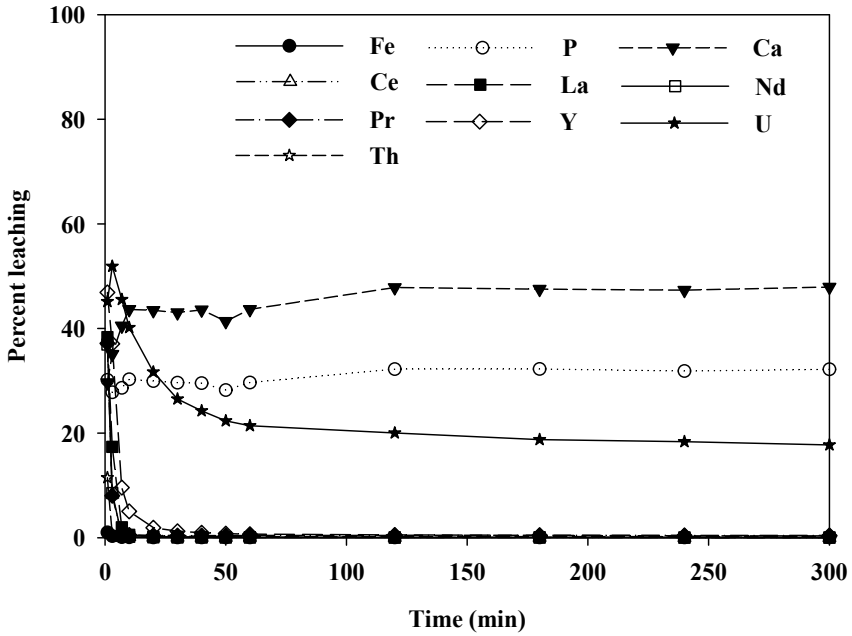

Figure 33. Change of leaching levels with time at 40 % of pulp density

4.7. Process proposal

From the results, the optimal REE leaching process of the HGZ ore can be proposed as shown in Figure 34. The ore is crushed to a size less than 1 mm and ground to 90 % passing size 50 mesh in a ball mill. The ground sample is subjected to magnetic separation in order to remove Fe bearing minerals.

The non-magnetic portion is used for the first leaching stage conducted at 25 ℃ with 2.0 M hydrochloric acid and 25 % pulp density. After leaching, impurity ions such as Ca, P, and U are removed by solid-liquid separation. The residue from the first leaching stage is subjected to the second leaching, which is conducted at 25 ℃ with 2.0 M hydrochloric acid and 10 % pulp density. The leachate from the second leaching stage is further processed to remove impurities by solvent extraction and to recover REE compounds by precipitation.

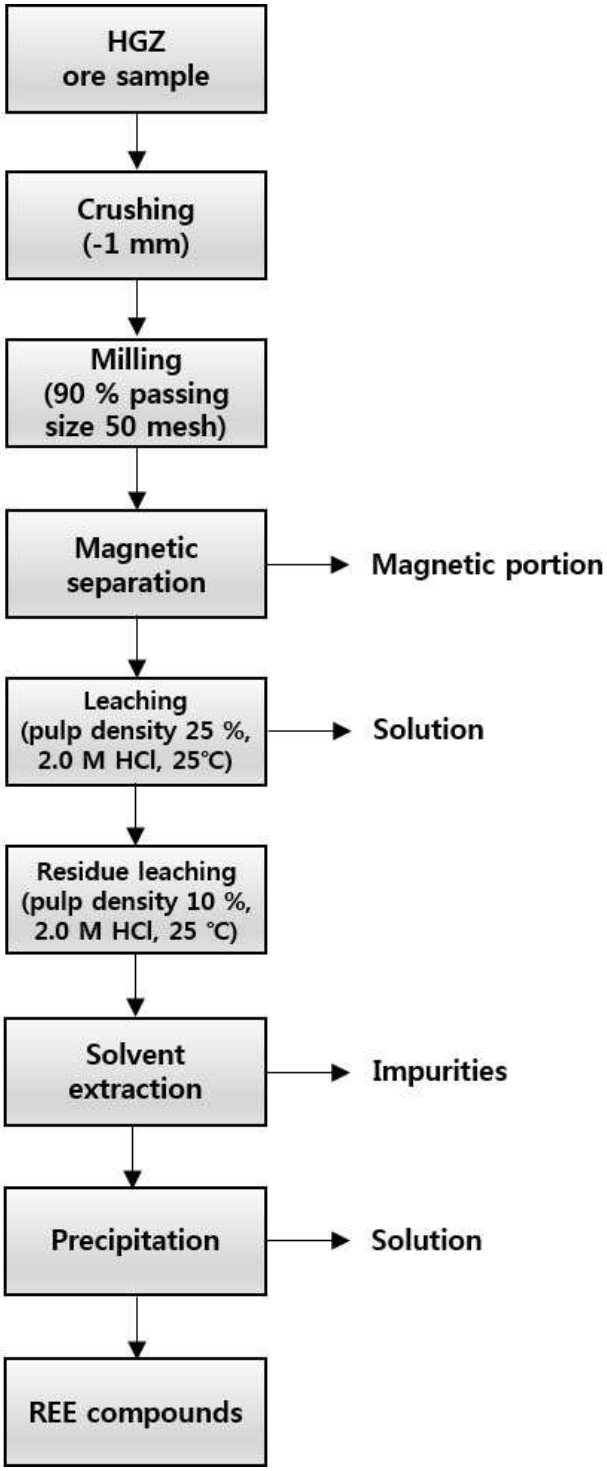

Figure 34. Proposed REE processing of the HGZ ore

5. Conclusion

A study determining the leaching characteristics of Rare Earth Elements (REE) ore from Mushgai Khudag, Mongolia, was conducted to help develop the REE processing technology. Sulfuric, hydrochloric, and nitric acids were used as leaching reagents looking at the effects of time, acid concentration, leaching reagent type, temperature, particle size, and pulp density on REE leaching levels. As a result, the optimum leaching conditions were established.

(1) Leaching kinetics

To determine the optimum leaching time for the HGZ sample, leaching experiments were performed with time. 13.0 M sulfuric acid as well as 2.0 M hydrochloric and nitric acid were used as leaching reagents. For sulfuric acid, the leaching levels decreased after 3 hrs probably due to the precipitation of REE with SO_4^{2-}. The leaching kinetics was very fast for all REE with less than 1 hr for maximum leaching levels with hydrochloric acid or nitric acid.

(2) Effect of acid concentration and type on leaching levels

To dissolve the target materials in ore, it is important to maintain a suitable acid concentration. The recovery of REE and the type of leaching products vary depending on the leaching reagent. When sulfuric acid was used as a leaching reagent, 70 ~ 80 % of REE leached out even at high acid

concentrations, due to the formation of sulfates. On the contrary, more than 90 % REE were recovered, when hydrochloric acid or nitric acid was used. However, hydrochloric acid is cheaper than nitric acid, and thus hydrochloric acid is a better leaching reagent.

(3) Effect of temperature on leaching levels

To determine the effect of temperature, leaching experiments were performed using 13.0 M sulfuric acid and 1.0 M hydrochloric acid as leaching reagents. With 13.0 M sulfuric acid, most REE leaching levels increased significantly up to over 80 % as temperature was increased to 80 ℃. For 1.0 M hydrochloric acid, REE leaching levels did not increase much as the temperature increased. Thus, 2.0 M hydrochloric acid and 25 ℃ are optimum conditions.

(4) Effect of magnetic separation

When leaching experiments were performed with the magnetic separated sample, leaching levels of REE remained high. The leaching levels of Fe were less than 10 % using both raw samples and separated samples. However, Fe concentration in the leachate after magnetic separation was just 60 ppm as compared to 260 ppm without magnetic separation. Therefore, it would be very beneficial to process the ore by magnetic separation prior to leaching.

(5) Effect of particle size

The cost of mineral processing is affected by comminution because this step is energy intensive. However, decreasing the particle size improves leachability and liberation degree. To study the effects of particle size in leaching experiments, 3 different particle sizes were tested: (1) 50 mesh (0.3 mm), (2) 100 mesh (0.15 mm), and (3) 200 mesh (0.075 mm). There was no big difference in the leaching levels of REE at varying particle sizes. Therefore, the 50 mesh particle size is the optimum.

(6) Effect of pulp density

As the pulp density increases, the amount of ore treated increases and leaching rate decreases. The optimum pulp density will allow for a more economical solution to the issue. At 10 % and 15 % pulp density, leaching levels increased to above 80 %, but impurities were also high. At 25 %, most REE disappeared and leaching levels of some impurities were high. This means that impurities could be removed by a solid-liquid separation. However, at 40 %, there was no benefit to recovering REE from the ore.

(7) Process proposal

From the results, the optimal REE leaching process of the HGZ ore can be proposed. The ore is crushed and ground to 90 % passing size 50 mesh. The ground sample is subjected to magnetic separation.

The magnetic separated sample is used for the first leaching stage conducted at 25 ℃ with 2.0 M hydrochloric acid and 25 % pulp density. After leaching, impurity ions in liquid phase are removed. The residue from the first leaching stage is subjected to the second leaching, which is conducted at 25 ℃ with 2.0 M hydrochloric acid and 10 % pulp density. The leachate from the second leaching stage is further processed by solvent extraction and precipitation.

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초 록

2010년 중국의 희토류 수출쿼터 축소 발표와 함께 중국과 일본간에 촉발된 센가쿠 열도 분쟁을 계기로 희토류 가격이 급등하면서 희토류 자원의 중요성이 부각되기 시작했다. 국내의 경우 희토류 가격이 저렴하던 시절 희토류 가공 기술 개발을 하지 않고 이웃 국가에서 희토류 완제품 또는 반제품을 수입하였다. 따라서 희토류 가격이 급등하자 다른 어느 나라보다도 타격이 컸다. 현재는 희토류 가격이 많이 하락하였으나 또 다시 같은 상황이 반복될 가능성이 있으므로 자원 안보 차원에서 희토류 자원에 대한 대책 마련이 필요하다. 이에 현재 국내에서는 희토류 광상 개발 관련 R&D가 진행중이다. 본 연구에서는 R&D 프로젝트 중 희토류 광석의 산 침출에 관한 연구를 수행하였다. 연구에 사용된 희토류 광석은 몽골 무시가이쿠닥 지역의 High Grade Zone에서 채취하였다. 이 지역의 희토류 광석 품위는 약 10 %로 높은 편에 속하므로 적절한 가공 기술이 적용된다면 국내에 다량의 희토류 공급이 가능해진다.

최적 희토류 침출 조건을 확립하기 위해 다양한 조건에 대한 실험을 수행하였다. 침출제로는 황산, 염산, 질산을 이용하였다. 연구에 사용된 광석의 기본적인 침출 특성 파악을 위해 세 가지 침출제를 사용하여 시간에 따른 침출율 변화에 대한 연구를 가장 먼저 수행하였다. 이 연구를 통해 침출 반응의 가능성과 최적 침출 시간을 도출해내었다. 이와 함께 각 침출제의 농도 변화에 따른 침출율 변화를 파악하여 최적 침출제 및 최적 침출 농도를 선정하였다.

침출 시간, 침출제, 침출 농도를 선정한 후에는 침출율 향상을 위한 연구를 수행하였다. 우선 온도 조절을 통한 침출율 향상 연구를 진행하였다. 온도가 증가하면 화학 반응의 속도 또한 증가할 수 있기 때문에 비교적 낮은 산 농도에서 온도를 상승시켜 실험해 볼 필

요성이 있다. 그리고 자력선별 된 시료를 이용하여 침출액 중 철분 제거 가능성을 파악하였다. 침출액 중에 다량의 철분이 포함되어 있을 경우 후속 공정에 많은 비용이 소요될 수 있기 때문이다. 또한 시료 입도를 변화시키면서 침출 실험을 수행하였다. 시료의 입도가 적정 수준으로 조절되면 광석의 단체 분리가 적절히 일어나 원하는 성분을 효율적으로 추출할 수 있다. 마지막으로 광액 농도의 변화에 따른 침출율 변화를 파악하였다. 고체 시료와 산 용액의 비율이 적절히 조절되면 최적 침출율을 얻는 동시에 경제적인 침출제 양을 도출할 수 있다.

실험 결과, 2.0 M의 염산 또는 질산이 사용되었을 때 1 시간 안에 90 % 이상의 희토류가 침출되었다. 황산이 침출제로 사용되었을 때는 13.0 M의 비교적 높은 농도의 산이 사용되었음에도 불구하고 희토류가 칼슘 황산염과 공침하여 70 ~ 80 %의 희토류만이 침출되었다. 따라서 최적 침출제는 2.0 M 염산으로 선정하였고 침출 시간은 1 ~ 2 시간으로 하였다. 온도 상승에 의한 희토류 침출율 향상 가능성은 미미한 것으로 나타나 최적 침출 온도는 상온으로 하였다. 또한 최적 시료 입도는 90 % passing size가 50 mesh (0.3 mm)가 되도록 하였다. 더 작은 입도에서도 실험을 수행하였으나 결과에 큰 차이가 없는 것으로 밝혀졌다. 희토류 침출에 대한 최적 광액 농도는 10 ~ 15 % 인 것으로 파악되었다. 그러나 광액 농도 25 %의 경우 1시간 내에 희토류가 침출액 내에서 사라지지만 불순물들의 침출액 내 농도는 높게 유지되기 때문에 고액분리를 통한 불순물 제거 가능성이 있을 것으로 보인다.

주요어 : 희토류, 산 침출, 아파타이트, 자력선별
학 번 : 2011-21090

감사의 글

지난 2011년 대학원에 입학하여 3년 만에 드디어 석사 졸업을 하게 되었습니다. 대학원 생활하는 동안 힘든 일도 많았지만 무사히 졸업하게 되어 매우 기쁘게 생각합니다. 이 자리에 있기까지 저에게 힘을 주신 모든 분들에게 감사를 드리고자 이 글을 씁니다.

학부 시절부터 지도교수님으로 지금까지 이끌어 주신 존경하는 조희찬 교수님! 부족한 점이 많은 저에게 습식제련과 희토류라는 전도유망한 분야의 연구를 할 수 있는 기회를 주시고 학문적으로, 또 인간적으로 많은 가르침을 주셔서 정말 감사드립니다. 대학교 신입생 때부터 석사를 졸업하는 지금까지 많이 방황했었는데 그때마다 아낌없이 해주셨던 조언들 덕분에 이 자리까지 올 수 있었습니다. 특히 지난 여름 진로 고민으로 막막해 하고 있을 때 먼저 저의 가능성을 보시고 박사과정으로 공부를 지속할 수 있도록 이끌어 주셔서 감사합니다. 그리고 지금은 미국에 계신 한국남 교수님께도 감사의 말씀 전하고 싶습니다. 습식제련 분야의 대가이신 교수님을 만나 뵙고 직접 가르침을 받을 수 있어 영광이었습니다. 교수님의 가르침 덕분에 저의 연구가 한층 더 발전할 수 있었습니다. 또한 바쁘신 와중에도 시간 내시어 논문 심사 해주신 민동주 교수님, 정은혜 교수님. 좋은 논문이 나올 수 있도록 많은 조언 해 주셔서 진심으로 감사드립니다. 실험에 도움을 주신 한국광물자원공사 유영준 팀장님, 윤미희 과장님, 이영재 선생님께도 감사드립니다.

그간 연구실 생활하면서 동고동락했던 연구실 식구들! 얼마전부터 권 교수님이 되신 지회오빠, 은근히 잘 챙겨주시는 지자연에 있는 관호오빠, 드디어 저와 함께 졸업하는 기홍오빠, 135동에 있어 잘 못 보지만 만나면 즐거운 명욱오빠, 우리 연구실 맥가이버 대양오빠, 연구실에서 함께 했던 유일한 '여자 선배님' 아라언니, 학부 학

번은 제각각이지만 연구실은 동기인 잘 생겼던 철호오빠와 든든한 정진안, 그리고 후배들 용태, 찬기, 정훈이, 마리오. 모두 감사합니다. 여러분 덕분에 지금까지 연구실 생활 참 즐거웠고 앞으로도 그랬으면 합니다.

그리고 아무것도 모르던 스무 살에 만나 지금은 어엿한 28살 청년들이 된 지환시 B반 06학번 동기들! 외로웠던 서울 생활 동기들이 있어서 행복했습니다. 지금은 각자 길 찾아가느라 자주 보지도 못 하고 첫 엠티 때처럼 다 모이기도 힘들어졌지만 카톡 대화방에서 나누는 대화만으로도 반갑고 때로는 힘이 됩니다. 다들 각자 위치에서 성공하길 바랍니다.

나의 부산 친구들! 친구지만 언니 같은 이제는 구미여자인 소자(그리고 률 오빠), 말은 안 해도 많이 의지하게 되는 방실이, 똑소리 나는 방돌이 엄마 정지, 은근 함께 한 것이 많은 나의 유럽여행 메이트 눈까리 새롬, 뛰어난 손재주가 부러운 펭, 고3 시절을 함께 한 은근 허당 배씨. 힘든 시기에 많은 힘이 되어 주었던 친구들 정말 고맙습니다. 저 또한 힘이 되는 친구가 되도록 하겠습니다.

마지막으로 사랑하는 가족, 친지들께도 감사의 말씀 전합니다. 우리집 막둥이 내 동생 지나. 많이 싸우기도 했지만 그래도 동생이 있어 외롭지 않았습니다. 그리고 누구보다 저를 예뻐해 주신 우리 할머니. 손녀딸 박사도 되고 결혼하는 모습도 보시도록 건강해지셨으면 좋겠습니다. 사랑해요, 할머니! 존경하고 사랑하는 엄마, 아빠! 큰 딸 이렇게 잘 키워주셔서 감사합니다. 실망시켜 드린 적도 있는데 그런 때조차도 큰 딸 믿고 지켜봐 주셔서 정말 감사합니다. 항상 엄마, 아빠 생각하며 매사 열심히 임해서 '꼭 필요한 사람'이 되겠습니다. 엄마, 아빠 완전 사랑합니다!

그리고 김재현, 고맙습니다.